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Monthly Variability and Possible Sources of Nitrate in Ground Water Beneath Mixed Agricultural Land Use, Suwannee and Lafayette Counties, Florida

U.S. GEOLOGICAL SURVEY
Water-Resources Investigations Report 00-4219

Prepared in cooperation with the
FLORIDA DEPARTMENT OF ENVIRONMENTAL PROTECTION

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By Brian G. Katz and J.K. Bohlke

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Monthly Variability and Possible Sources of Nitrate in Ground Water Beneath Mixed Agricultural Land Use, Suwannee and Lafayette Counties, Florida

By Brian G. Katz *and* J.K. Bohlke

Abstract

In an area of mixed agricultural land use in Suwannee and Lafayette Counties of northern Florida, water samples were collected monthly from 14 wells tapping the Upper Floridan aquifer during July 1998 through June 1999 to assess hydrologic and land-use factors affecting the variability in nitrate concentrations in ground water. Unusually high amounts of rainfall in September and October 1998 (43.5 centimeters total for both months) resulted in an increase in water levels in all wells in October 1998. This was followed by unusually low amounts of rainfall during November 1998 through May 1999, when rainfall was 40.7 centimeters below 30-year mean monthly values.

The presence of karst features (sinkholes, springs, solution conduits) and the highly permeable sands that overlie the Upper Floridan aquifer provide for rapid movement of water containing elevated nitrate concentrations to the aquifer. Nitrate was the dominant form of nitrogen in ground water collected at all sites and nitrate concentrations ranged from less than 0.02 to 22 milligrams per liter (mg/L), as nitrogen. Water samples from most wells showed substantial monthly or seasonal fluctuations in nitrate concentrations. Generally, water samples from wells with nitrate concentrations higher than 10 mg/L showed the greatest amount of monthly fluctuation. For example, water samples from six of eight wells had monthly nitrate concentrations that varied by at least 5 mg/L during the study period. Water from most wells with lower nitrate concentrations (less than 6 mg/L) also showed large monthly fluctuations. For instance, nitrate concentrations in water from four sites showed monthly variations of more than 50 percent. Large fluctuations in nitrate concentrations likely result from seasonal agricultural practices (fertilizer application and animal waste spreading) at a particular site. For example, an increase in nitrate concentrations observed in water samples from seven sites in February or March 1999 most likely results from application of synthetic fertilizers during the late winter months.

Lower nitrate concentrations were detected in water samples from five of eight wells sampled during high-flow conditions for the Suwannee River in March 1998 compared to low-flow conditions in November 1998. Evidence for reduction of nitrate due to denitrification reactions was observed at one site (AC-1), as indicated by elevated concentrations of nitrogen gas and a corresponding increase in nitrogen isotope ($\delta^{15}N\text{-}NO_3$) values with a decrease in nitrate concentrations. Denitrification is unlikely at other sites based on the presence of dissolved oxygen concentrations greater than 2 mg/L in ground water and no observed trend between nitrate concentrations and values $\delta^{15}N\text{-}NO_3$ values.

Nitrate was the dominant nitrogen species in most monthly rainfall samples; however, ammonium concentrations were similar or greater than nitrate during November and December 1998.

During February through May 1999, both nitrate and ammonium concentrations were substantially higher in monthly rainfall samples collected at the study area compared to mean monthly concentrations at the Bradford Forest site located east of the study area, which is part of the National Atmospheric Deposition Program/National Trends Network. Also, higher nitrogen deposition rates in the study area compared to those at Bradford Forest could indicate that substantial amounts of ammonia are volatilized from fertilizers and animal wastes, released to the atmosphere, and incorporated as nitrate and ammonium in rainfall deposited in the middle Suwannee River Basin.

Ground-water samples from most sites had $\delta^{15}N\text{-}NO_3$ values that indicated a mixture of inorganic and organic sources of nitrogen, which corresponded to multiple land uses where both synthetic fertilizers and manure are used on fields near these sites. Distinct $\delta^{15}N\text{-}NO_3$ signatures, however, were observed at some sites. For example, water samples from areas of row-crop farming as the dominant land use had $\delta^{15}N\text{-}NO_3$ values less than 4 per mil, indicating an inorganic nitrogen source such as synthetic fertilizer. In contrast, $\delta^{15}N\text{-}NO_3$ values greater than 9 per mil were found in water samples from three sites where manure from dairy and or poultry operations is spread on fields throughout the year.

INTRODUCTION

Elevated nitrate concentrations in ground water constitute an important ecological and human-health concern in the middle Suwannee River Basin (MSRB) in Florida (fig. 1). Water from the Upper Floridan aquifer, the main source of water supply in this area, and discharge of ground water from large springs contribute substantial amounts of nitrogen and flow to the Suwannee River (Pittman and others, 1997; Hornsby and Ceryak, 1999). Numerous domestic and monitoring wells that tap the Upper Floridan aquifer yield water with nitrate concentrations that exceed 10 milligrams per liter (mg/L) as nitrogen, the maximum contaminant level set by the U.S. Environmental Protection Agency. Nitrate concentrations greater than 10 mg/L as nitrogen can cause methemoglobinemia in infants (Mueller and Helsel, 1996). Nitrate concentrations in this report are expressed in milligrams per liter as nitrogen and hereafter will be referred to as nitrate-N.

Identification of the sources of nitrate and understanding the natural variability of nitrate concentrations in ground water are important in developing effective management practices to prevent further degradation of water quality. At present, some information exists on the sources of nitrate in the Upper Floridan aquifer in parts of the Suwannee River Basin, but little information exists on the temporal variability of nitrate concentrations in ground water beneath different types of land use. Knowing the degree of variability of nitrate concentrations in ground water is important to properly evaluate the effect of best management practices (BMPs) on water quality. If large variations in nitrate concentrations are observed over a short timeframe, such as monthly, due to hydrologic and other factors, then this variability may make it difficult to discern improvements in water quality due to the implementation of BMPs for the various land-use types. The occurrence of many possible sources of nitrate from various agricultural land-use activities in the basin in close proximity to each other also makes it difficult to determine the relation between nitrate concentrations in ground water and the temporal variability of nitrate introduced from one or more sources. Previous studies have identified animal wastes associated with dairy (Andrews, 1994) and poultry farming operations (Hatzell, 1995) and fertilizers applied to cropland (Hornsby, 1994; Katz and others, 1999) as important sources of nitrate to ground water in the Suwannee River Basin.

Purpose and Scope

This report describes the results of a cooperative study between the Florida Department of Environmental Protection (FDEP) and the U.S. Geological Survey (USGS) that was designed to evaluate sources of nitrate contamination and temporal variability of nitrate concentrations in the Upper Floridan aquifer. During July 1998 through June 1999, water samples were collected monthly from 14 wells open to shallow zones of the Upper Floridan aquifer in the MSRB in northern Florida. Also, during this period, rainfall was collected monthly from a wet/dry atmospheric deposition collector in Suwannee County to evaluate temporal variability in nitrogen species. Water samples were collected during low-flow (base flow) conditions (November 1998) for the Suwannee River and analyzed for

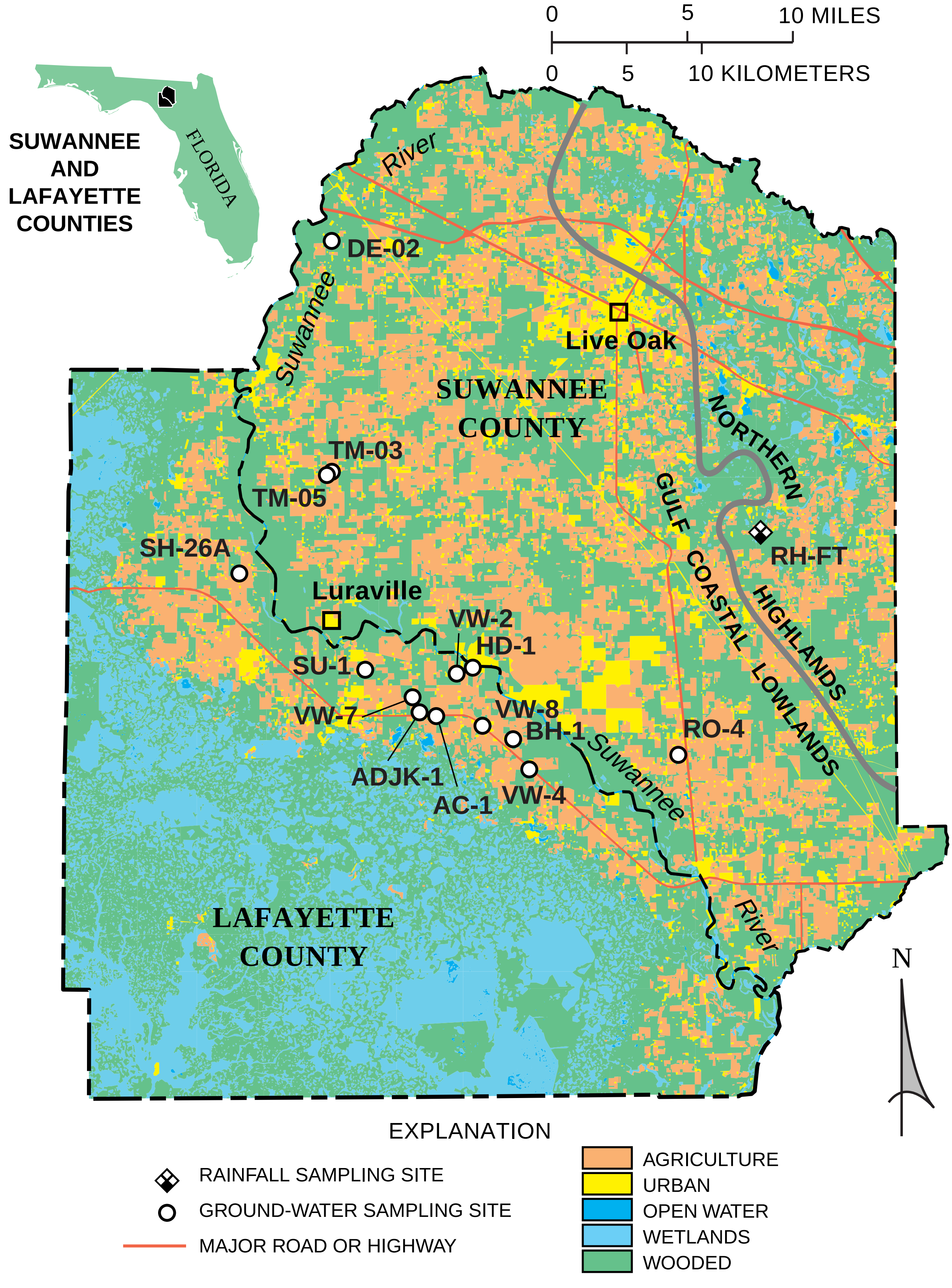

Figure 1. Location of sampled wells, rainfall collector at Rocky Hill Fire Tower (RH-FT), and 1995 land-use coverage in Suwannee and Lafayette Counties, Florida.

nitrogen isotopes to determine sources of nitrate in ground water. The study also was designed to collect ground-water samples during high-flow conditions of the river in the spring of 1999, but due to unusually low amounts of rainfall during January through May, no high-flow conditions were observed. Water samples were collected, however, during high-flow conditions in March 1998 as part of another study at eight of the 14 wells that were sampled during July 1998 through June 1999. Chemical and isotopic data for water samples from these eight wells are compared with data from November 1998 to relate nitrate concentrations to large differences in ground-water levels, and to evaluate geochemical processes that affect changes in nitrate concentrations during low-flow and high-flow conditions of the Suwannee River.

Previous Studies

Since 1987, detailed information on ground-water quality in Suwannee and Lafayette Counties has been collected as part of the Florida Ground Water Quality Monitoring Program (FGWQMP), which was established to delineate the baseline or background water quality of the major aquifer systems within Florida and to determine the effects of various land-use activities on ground-water quality. The 107 FGWQMP wells, which were sampled to monitor background water quality of the principal aquifers in the Suwannee River watershed, were selected to avoid known areas of ground-water contamination. Water samples were collected from these wells every 3 years and analyzed for major ions, nutrients, trace elements, and selected organic compounds (Maddox and others, 1992). Background nitrate-N concentrations in ground water were less than 0.05 mg/L (Katz, 1992; Maddox and others, 1992).

As part of the State monitoring program, effects of agricultural land use on water quality were evaluated in a 73-kilometer squared (km^2) study area adjacent to the Suwannee River in Lafayette County (Maddox and others, 1998). The study area consists mainly of agricultural land use, such as dairy and poultry farms, cropland, and silviculture. In April-May 1990, March 1991, and June 1994, water samples from 18 wells tapping the Upper Floridan aquifer and 7 springs that discharge water into the Suwannee River were analyzed for nitrate and other chemical constituents. Median nitrate-N concentrations for water samples collected in 1990, 1991, 1994, and 1997 were about 2 mg/L compared to the background concentration of nitrate-N of 0.20 mg/L for water samples from 43 background network wells in the MSRB (Maddox and others, 1998). Based on a comparison of ground-water chemistry in 1991 with that in 1990, conditions favorable for the natural reduction of nitrate in ground water by denitrification reactions were noted and were related to the following conditions: a sluggish ground-water flow system, substantially reduced amounts of dissolved oxygen in the aquifer, and increased amounts of organic carbon and other reduced species that could serve as electron donors (Katz and others, 1997).

Approximately 500 domestic wells were sampled in a 260 km^2 study area in northeastern Lafayette County between June and September 1998 (Copeland and others, 1999). Water from wells located within 100 meters (m) of poultry and dairy operations had a median nitrate-N concentration of 3.7 mg/L, which was significantly higher ($p=0.002$) than for ground water beneath areas classified as background (Copeland and others, 1999).

Several studies have used nitrogen isotopes to assess sources of nitrate in ground water. In Lafayette County, the principal source of nitrate in ground water discharging from springs to the Suwannee River was attributed to a combination of leachate from livestock wastes and septic tanks, based on measured nitrogen-isotope ratios of nitrate ($\delta^{15}N-NO_3$) in water samples collected in May 1993 (Andrews, 1994). Based on nitrogen isotope analyses of water from 66 monitoring and drinking-water wells in the MSRB, Hornsby (1994) determined that water from four wells produced $\delta^{15}N-NO_3$ values that were equal to or greater than 10 per mil, indicating an organic nitrogen source. Three of these four wells were located downgradient from dairy or poultry operations, indicating the likelihood of localized sources of animal wastes. The majority of wells (44 of 66) yielded water with $\delta^{15}N-NO_3$ values that were less than or equal to 2 per mil, indicating that inorganic nitrogen (synthetic fertilizers) and (or) soil nitrogen was the dominant source of nitrate in the MSRB (Hornsby, 1994). The depth of the 66 wells ranged from 14 to 44 m below land surface.

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DESCRIPTION OF STUDY AREA

The middle Suwannee River Basin in Florida is characterized by karstic wetland and lowland topography, a small number of tributary streams, and an abundance of Upper Floridan aquifer springs. The climate in the study area is subtropical and is characterized by long, warm summers and mild winters. Rainfall averages 132 centimeters (cm) per year (Crane, 1986); however, there are large variations between locations and from year to year. Approximately 50 percent of the average annual rainfall occurs from June through September, but the shorter rainy season from late February through late April typically produces some of the highest stages for the Suwannee River and its tributaries because of high evapotranspiration during summer months.

Land Use in Suwannee and Lafayette Counties

Major land uses in the Suwannee River Basin include forest, wetlands, and agriculture, which includes cropland, pastures, and confined animal-feeding operations (poultry, livestock, and swine). The percentage of land-use types in Lafayette and Suwannee County also varies considerably (table 1). The percentage of agricultural land use has decreased in both counties based on a comparison between mid-1970 and 1995 data, which was obtained from a land-use and land-cover classification system for remote sensor data (Anderson and others, 1976; Mitchell and others, 1977). In Lafayette and Suwannee Counties, respectively, agricultural land accounted for 15 and 47 percent (1977) and 11 and 35 percent (1995). Forested land remained at about 50 percent in both counties in 1977 and 1995. Much of the forested land is planted by the paper industry for silviculture. In Lafayette and Suwannee Counties, respectively, wetlands accounted for about 36 and 2 percent in 1995; urban land use increased from 0 to 2 percent and from 1 to 9 percent between 1977 and 1995, respectively (table 1).

Table 1. Percentage of land-use types in Lafayette and Suwannee Counties, 1977 and 1995

[km^2, square kilometers]

County (area in km^2)	Year	Land use, in percent				
		Agriculture	Forest	Urban	Wetlands	Other
Lafayette (1,412)	1977	15	51	0	33	1
	1995	11	49	2	36	2
Suwannee (1,786)	1977	47	49	1	1	2
	1995	35	52	9	2	2

Hydrogeologic Framework

The major hydrogeologic units in the middle Suwannee River Basin, in descending order, include the surficial aquifer system, the intermediate confining unit, and the Upper Floridan aquifer. The surficial aquifer system, which consists of undifferentiated sands and clays of post Miocene age, ranges in thickness from 3 to 10 m, but can be 15 to 18 m in the easternmost part of the basin (Scott, 1991). The intermediate confining unit is composed of siliclastic sediments of Miocene age, and is present only under the Northern Highlands physiographic region in the northeastern part of Suwannee County. The thickness of the confining unit in this region can exceed 100 m (Scott, 1988). The Upper Floridan aquifer, the uppermost part of the Floridan aquifer system, consists of limestone and dolomite of Eocene age. This aquifer is the primary source for industrial, agricultural, and municipal water use in the Suwannee River Basin in Florida. The base of potable water in the Upper Floridan aquifer ranges from approximately 300 m below land surface in the southern part of the study area to more than 380 m below land surface in the northern part of the study area (Ceryak and others, 1983). Solution features (sinkholes, solution conduits, springs) characteristic of karst areas provide the opportunity for direct hydraulic and geochemical interactions between surface water and ground water in the basin.

The hydrogeology within the Suwannee River Basin is directly related to the physiography. The northern part of the basin is located in the Northern Highlands, a region characterized by land-surface altitudes ranging from 30 to 70 m. Surface-water features are common in this region because clayey sediments of the intermediate confining unit underlie the surficial aquifer system and retard the infiltration of rainwater. Water levels of surface-water features reflect the water table in the surficial aquifer system. The southern part of the study area lies in the Gulf Coastal Lowlands physiographic division, which is characterized by land altitudes that are less than 30 m and the presence of carbonate rock at or near land surface.

The Northern Highlands and Gulf Coastal Lowlands are separated by a topographic break referred to as the Cody Scarp (Puri and Vernon, 1964). With the exception of the Suwannee River, every river or stream that originates in the Northern Highlands disappears underground as it crosses this transition zone. The Suwannee River remains above ground in the Gulf Coastal Lowlands because it has incised the limestone of the Upper Floridan aquifer.

The Upper Floridan aquifer in the MSRB is extremely permeable and capable of transmitting large amounts of water (Bush and Johnston, 1988). Recharge rates to the aquifer are controlled by the degree of confinement of the aquifer, and range from less than 30 to 80 centimeters per year (cm/yr) in areas where the aquifer is confined or unconfined, respectively (Grubbs, 1998). In the MSRB, discharge from the aquifer to springs and to the Suwannee River occurs where the hydraulic head of the aquifer is above land surface. Based on the potentiometric surface of the Upper Floridan aquifer in the Suwannee River Water Management District (Mahon and others, 1997), the direction of regional ground-water flow in Suwannee County generally is south to southwestward toward the Suwannee River; in Lafayette County, the flow generally is east to northeast toward the Suwannee River. The direction of local ground-water flow can vary considerably from the regional ground-water flow directions determined from potentiometric-surface maps (Hatzell, 1995). Local variations in ground-water flow directions are related to land use, thickness of confining units overlying the Upper Floridan aquifer, variability in recharge to the aquifer, and aquifer properties.

METHODS

From July 1998 through June 1999, water samples were collected monthly from 14 wells open to shallow zones of the Upper Floridan aquifer in the MSRB in northern Florida. Of the 14 wells, 9 were monitoring wells and 5 were domestic wells. These wells were chosen based on their location along ground-water flow paths toward the Suwannee River. Well construction information is provided in table 2.

Collection and Analysis of Ground-Water Samples

Water samples from wells were collected after a minimum of three well-bore volumes of water had been purged and readings of specific conductance, pH, dissolved oxygen, and temperature of the ground water had stabilized. A closed flow-through chamber was used to measure these water properties to prevent contact of the ground water with the atmosphere. Samples of ground water were collected monthly and analyzed for major nitrogen species including nitrite, nitrate, total Kjeldahl nitrogen (TKN, which represents organic nitrogen plus ammonia) and ammonia. Nitrite plus nitrate concentrations are reported by the laboratory; however, nitrite concentrations in ground water typically are below detection limits (Katz, 1992; Andrews, 1994), so these analyses can be considered to represent only nitrate. All nitrogen species are reported as elemental nitrogen in this report. During March and November 1998, samples from selected wells were collected and analyzed for major ions, nutrients, dissolved organic carbon (DOC), and selected environmental isotopes including tritium (^{3}H), deuterium (^{2}H), oxygen-18 (^{18}O), carbon-13 (^{13}C), and nitrogen-15 (^{15}N).

Water samples were collected for analysis of major element chemistry and DOC using standard techniques (Koterba and others, 1995) that included field filtration with a 0.45-micron (µm) membrane filter for major ions, nutrients, and silica, and a 0.45-um silver filter for DOC. These samples were kept chilled at 4 degrees Celsius (^{o}C) in the field and analyzed in the USGS laboratory in Ocala, Fla., using standardized procedures (U.S. Geological Survey, 1999). To ensure consistency in sampling methodology from month to month, every attempt was made to use the same field crew and equipment (submersible pump for wells without an in-line pump, meters for measuring pH, specific conductance, temperature, and dissolved oxygen), and flow-through cell.

Isotopic values are reported using standard δ (delta) notation (Gonfiantini, 1981), as defined by the following expression: δ (in per mil) = $[(R_{sample}/R_{standard}) - 1] \times 1{,}000$. For $\delta^{18}O$, R = $^{18}O/^{16}O$; for δD, R = $^{2}H/H$; for $\delta^{13}C$, R = $^{13}C/^{12}C$; and for $\delta^{15}N$, R = $^{15}N/^{14}N$. Results for oxygen and hydrogen isotopes are reported in per mil relative to Vienna Standard Mean Ocean Water, and are normalized on scales such that the oxygen and hydrogen isotopic values of Standard Light Antarctic Precipitation are -55.5 per mil and

Table 2. Location information for sampled wells and description of land use of each site

[Elevations are reported in meters above sea level; Well depth and casing depth, in meters below land surface; Casing diameter, centimeters; km denotes kilometers; NA not applicable; ID, identification number; °, degrees; ′, minutes; ″, seconds; m, meters]

Site Name	Local site ID	Latitude	Longitude	Land surface elevation	Measuring point elevation	Well Depth	Casing depth	Casing diameter	Land use near sampled site
VW-2	-051203002	30°04′43″	83°05′57″	14.94	14.45	16.76	7.62	10	Pasture, planted pines, highway ditch within 100 m of well; poltry houses and dairy about 1.6 km
VW-4	-051330005	30°01′14″	83°02′59″	15.24	14.75	14.33	8.23	10	Pasture and row crops, highway within 100 m of well; poultry houses, planted pines, pasture, dairy cattle within 1.6 km from well
VW-7	-051209001	30°03′51″	83°07′48″	17.98	17.68	13.41	7.32	10	Pasture, planted pines, beef cattle within 100 m of well; dairy, low density residential, and pasture within 1.6 km of well
VW-8	-051214008	30°02′49″	83°04′53″	15.54	15.17	15.85	6.71	10	Pasture, hay field, highway within 100 m of well; dairy and poultry houses within 1.6 km of well
RO-4	W-17269	30°01′45″	82°56′45″	15.58	16.21	13.11	10.97	10	Cropland, single residence within 100 m of well
BH-1	-051319001	30°02′20″	83°03′36″	14.63	14.92	23.16	12.19	10	Single residence with septic tank, lined catfish pond, pasture, dairy calves, silviculture within 100 m of well
AC-1	-051216011	30°03′10″	83°06′50″	18.59	19.05	32.00	25.60	10	Four residences with septic tank within 100 m of well; dairy barns and poultry houses within 1.6 km of well
ADJK-1	-051216006	30°03′19″	83°07′03″	21.34	21.64	16.15	11.28	10	Dairy calf pens within 100 m; several mobile homes with septic tank(s), pasture; within 1.6 km rural agricultural and high intensity dairy farming, silviculture; low population density
SU-1	-051206001	30°04′50″	83°09′44″	19.81	20.12	18.29	16.76	10	Poultry broiler houses; residence with septic tank; tobacco driers, fertilizer spreaders, farm equipment storage within 100 m of well
HD-1	-051202002	30°04′55″	83°05′15″	13.11	13.51	19.81	18.29	10	Residence and septic tank within 100 m of well
SH-26A	L2-6A	30°08′19″	83°15′00″	22.25	23.04	14.63	11.58	10	Dairy farming operation; sprayfield within 100 m of well
TM-05	TM-05	30°11′54″	83°11′19″	24.38	25.21	19.51	16.46	5	Poultry broiler houses; residence with septic tank; tobacco driers, fertilizer spreaders, farm equipment storage within 100 m of well
TM-03	TM-03	30°11′57″	83°11′13″	23.47	24.26	18.59	15.54	5	Same as TM-05
DE-02	DE-02	30°20′17″	83°11′12″	22.56	23.34	19.51	16.46	5	poultry broiler houses near well
ROCKY HILL FT	RHFT	30°09′51″	82°53′18″	NA	NA	NA	NA	NA	Forested, with small amount of cropland in area

–428 per mil, respectively (Coplen, 1994). The 2σ precision of delta oxygen-18 ($\delta^{18}O$) and delta deuterium ($\delta^{2}H$) results is 0.2 and 2 per mil, respectively. The 2σ precision for the analytical procedure is 0.2 per mil (Coplen, 1994).

Samples for analysis of $\delta^{13}C$ in dissolved inorganic carbon (DIC) were collected by direct precipitation in the field by the addition of ammoniacal-$SrCl_2$ solution, followed by filtering, drying, and acidifying the resulting $SrCO_3$ precipitate to produce CO_2, which was analyzed by mass-spectrometric methods (Hassan, 1982). Values of $\delta^{13}C$ are reported relative to Vienna Pee Dee Belemnite (VPDB) (Coplen, 1994). Stable isotope analyses of water samples were performed by the USGS Isotope Fractionation Laboratory, Reston, Va. Values of $\delta^{13}C$ were determined by mass spectrometry and are reported as the per mil deviation from the VPDB standard (Coplen, 1994).

Water samples for nitrogen isotope analysis were filtered (0.45 um) into 1-liter plastic bottles and kept chilled at $4^{o}C$. Analytical techniques are described by Bohlke and Denver (1995) and Bohlke and Coplen (1995). Delta ^{15}N values for nitrate concentrations above 0.5 mg/L as nitrogen are normalized to values of +0.4 per mil for the International Atomic Energy Agency standard-N1 and +180.0 per mil for USGS-32 (Bohlke and Coplen, 1995), with analytical uncertainties of approximately ± 0.1 per mil.

Collection and Analysis of Rainfall Samples

Rainfall in the study area was measured at the Rocky Hill Fire Tower site (RH-FT) (fig. 1). Daily rainfall at this site was recorded using a tipping-bucket raingage. Monthly composited samples of rainfall were collected using an Aerochemetrics 301 wet/dry atmospheric deposition collector. Field measurements of pH and specific conductance were made on an aliquot of rainfall from each sample collected monthly from the wet/dry collector. Monthly composite samples of rainfall were analyzed for nitrogen species at the USGS laboratory in Ocala, Fla.

Data Analysis

Hypothesis tests were used to determine if observed differences in nitrate concentrations or water levels are due to random variability or statistically significant variations in populations. Spearman's Rho statistic was used to determine the degree of correlation between nitrate concentrations with ground-water levels, pH, specific conductance, and dissolved oxygen. This nonparametric statistic measures the strength of an increasing or decreasing relation between two variables (Iman and Conover, 1983). Observations were ranked so that any extreme values would not have a disproportionate effect on the correlation. A positive or negative relation between two variables was considered significant at an alpha value, or level of significance, of 0.05 or less.

MONTHLY CHANGES IN GROUND-WATER LEVELS

Water levels in observation wells and private wells were measured monthly to evaluate the response of the water-table elevation to rainfall and recharge. In response to heavy rainfall (43.51 cm) in September (31.67 cm) and October 1998 (11.84 cm), ground-water levels in all wells increased in October (fig. 2.) This unusually large amount of rainfall in September and October exceeded the mean monthly values at Live Oak, Fla., for 1961-90 (Owenby and Ezell, 1992) by 19.58 and 6.53 cm, respectively. Ground-water levels in October 1998 increased nearly 2 m in four wells: SH-26A, DE-02, HD-1, and VW-2. Eight other wells showed a smaller increase (fig. 2). Ground-water levels were lower at the end of the study period than at the beginning at most sites. During the remainder of the study period, monthly rainfall was well below mean monthly rainfall values. In fact, from November 1998 through May 1999, total rainfall was 40.74 cm below mean monthly rainfall values for these same months during 1961-90 at Live Oak. Typical increases in ground-water levels during the spring months of 1999 never occurred due to these below-normal amounts of rainfall from February through May 1999.

Variations in water-level trends among sites most likely are related to localized differences in recharge, topography, pumping from nearby water-supply wells, possible exchanges of water between the Suwannee River and the Upper Floridan aquifer during high-flow conditions, and the presence of nearby sinkholes. Large changes in water levels were noted for wells that were located near sinkholes in a pasture, and these changes were attributed to a direct hydraulic connection between the land surface and water in deeper parts of the aquifer in Suwannee County (Hatzell, 1995).

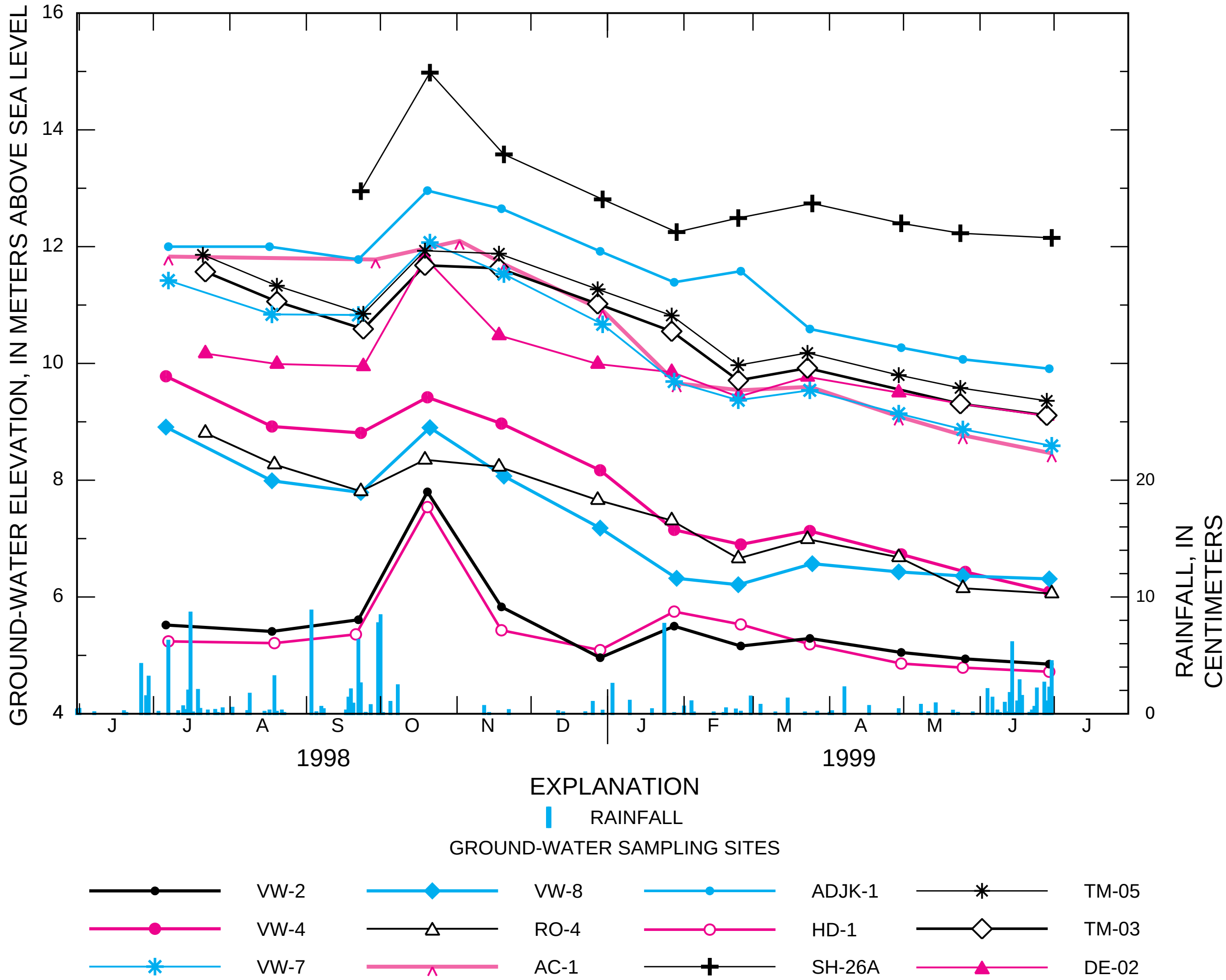

Figure 2. Changes in ground-water levels in sampled wells, Suwannee and Lafayette Counties, July 1998 to June 1999.

MONTHLY CHANGES IN CHEMISTRY OF GROUND WATER AND RAINFALL

Monthly values are presented in table 3 for ground-water characteristics measured in the field: pH, specific conductance, water temperature, and dissolved oxygen. The overall median and range of monthly median values, respectively, were pH 7.42 (7.20-7.67), specific conductance 360 uS/cm (335-386 uS/cm), temperature 22.2 ^{o}C (21.5-22.5 ^{o}C), and dissolved oxygen 4.8 mg/L (3.8 to 4.9 mg/L). Even though specific conductance and dissolved-oxygen concentrations fluctuated substantially from month to month in ground water at some sites (for example, at sites VW-4 and SU-1, table 3), pH was the only field measurement that showed statistically significant differences in monthly values ($p<0.05$). Median pH values ranged from 7.20 in May 1999 to 7.68 in August 1998. Monthly median pH values were lower than 7.40 for July, September, and December 1988, and for February, May, and June 1999. Monthly median pH values were higher than 7.40 for August, October, November 1998 and for March and April 1999. Fluctuations in monthly pH values likely are related in part to inconsistent sampling methods (alternate personnel using different meters and probes during the study period due to equipment failures).

Table 3. Chemical characteristics and nitrogen species concentrations of monthly ground-water and rainfall samples, and ground-water altitudes for sampled wells

[Units are as follows: °C, degrees Celsius; pH, standard units; SC 9specific conductance) in microsiemens per centimeter; DO (dissolved oxygen) and nitrogen species, milligrams per liter; ND, not determined; NA, not applicable; and RH-FT, Rocky Hill Fire Tower rainfall site]

Site Name	Sample Date	Water tempera-ture, °C	pH	SC	DO	Ammonium Nitrogen	Total Kjeldahl Nitrogen	Nitrate Nitrogen	Ground-water elevation, meters above sea level
VW-2	07/06/98	23.8	7.34	334	0.17	0.14	<0.2	0.02	5.52
VW-2	08/18/98	25.0	7.88	333	0.10	0.12	<.2	0.29	5.41
VW-2	09/22/98	23.2	7.29	346	0.39	0.12	<.2	1.2	5.61
VW-2	10/20/98	23.0	7.43	341	0.35	0.09	<.2	0.74	7.80
VW-2	11/19/98	23.2	7.30	338	0.10	0.10	0.26	0.51	5.83
VW-2	12/29/98	22.9	7.32	ND	0.10	0.11	0.22	<0.02	4.96
VW-2	01/28/99	23.1	7.36	344	0.20	0.10	<.2	0.93	5.50
VW-2	02/24/99	23.0	7.35	338	0.10	0.10	<.2	0.49	5.16
VW-2	03/24/99	23.2	7.54	334	0.20	0.10	<.2	0.28	5.29
VW-2	04/30/99	23.0	7.61	330	0.20	0.10	<.2	<0.02	5.05
VW-2	05/26/99	23.4	7.15	330	0.20	0.09	<.2	<0.02	4.94
VW-2	06/29/99	23.3	7.22	329	0.15	0.09	<.2	<0.02	4.85
VW-4	07/06/98	22.6	7.19	362	3.81	0.28	<.2	3.7	9.78
VW-4	08/18/98	21.4	7.61	364	3.30	<0.01	0.22	3.9	8.92
VW-4	09/23/98	22.4	7.41	364	3.35	0.01	<.2	4.1	8.81
VW-4	10/20/98	22.5	7.46	370	3.00	<0.01	<.2	4.3	9.42
VW-4	11/19/98	22.5	7.45	370	3.10	<0.01	<.2	4.2	8.97
VW-4	12/29/98	22.5	7.29	ND	2.70	<0.01	<.2	4.6	8.17
VW-4	01/28/99	22.7	7.64	376	2.90	<0.01	<.2	4.7	7.15
VW-4	02/24/99	22.5	7.06	381	2.90	0.01	<.2	5.1	6.90
VW-4	03/24/99	22.8	7.59	383	3.10	0.01	<.2	5.4	7.13
VW-4	04/30/99	22.1	7.62	386	3.20	0.01	<.2	4.7	6.73
VW-4	05/26/99	22.7	7.05	384	3.60	<0.01	<.2	5.0	6.43
VW-4	06/29/99	22.6	7.26	330	6.20	0.03	<.2	3.5	6.09
VW-7	07/07/98	22.6	7.15	549	4.75	0.03	<.2	14	11.42
VW-7	08/18/98	21.8	7.76	535	5.02	<0.01	<.2	17	10.84
VW-7	09/22/98	22.5	7.35	529	4.65	0.01	<.2	17	10.83
VW-7	10/21/98	22.6	7.31	522	4.60	<0.01	<.2	15	12.07
VW-7	11/20/98	23.0	7.43	542	4.40	<0.01	.34	17	11.53
VW-7	12/30/98	22.2	6.86	579	3.40	<0.01	0.22	20	10.67
VW-7	01/28/99	23.0	7.06	584	3.90	<0.01	<.2	19	9.69
VW-7	02/23/99	22.7	7.25	594	3.90	0.01	<.2	22	9.37
VW-7	03/24/99	23.0	7.41	600	3.70	0.01	<.2	21	9.54
VW-7	04/29/99	22.8	7.30	560	3.70	<0.01	<.2	18	9.14
VW-7	05/25/99	23.1	7.37	504	3.50	<0.01	<.2	16	8.87
VW-7	06/30/99	22.9	7.54	452	3.90	0.03	<.2	12	8.59
VW-8	07/06/98	22.4	7.41	315	1.35	0.03	<.2	3.8	8.91
VW-8	08/18/98	20.8	8.07	315	1.10	<0.01	<.2	3.7	7.99
VW-8	09/23/98	21.6	7.69	318	1.10	<0.01	<.2	3.8	7.79
VW-8	10/21/98	21.6	7.63	320	1.10	<0.01	<.2	3.8	8.90
VW-8	11/20/98	21.7	7.64	324	1.20	<0.01	<.2	3.7	8.07
VW-8	12/29/98	21.6	7.44	ND	1.10	0.02	<.2	3.1	7.18
VW-8	01/29/99	25.0	7.54	326	1.40	<0.01	<.2	2.9	6.32
VW-8	02/23/99	21.8	7.60	325	1.40	0.01	<.2	3.0	6.21
VW-8	03/25/99	21.9	7.65	330	1.90	0.02	<.2	3.1	6.57

Table 3. Chemical characteristics and nitrogen species concentrations of monthly ground-water and rainfall samples, and ground-water altitudes for sampled wells

[Units are as follows: °C, degrees Celsius; pH, standard units; SC 9specific conductance) in microsiemens per centimeter; DO (dissolved oxygen) and nitrogen species, milligrams per liter; ND, not determined; NA, not applicable; and RH-FT, Rocky Hill Fire Tower rainfall site]

Site Name	Sample Date	Water temperature, °C	pH	SC	DO	Ammonium Nitrogen	Total Kjeldahl Nitrogen	Nitrate Nitrogen	Ground-water elevation, meters above sea level
VW-8	04/29/99	22.4	7.62	334	2.30	<0.01	<.2	2.9	6.43
VW-8	05/25/99	22.4	7.52	335	2.30	<0.01	<.2	2.9	6.36
VW-8	06/29/99	22.2	7.35	338	2.40	0.02	<.2	2.8	6.31
RO-4	07/22/98	21.0	7.12	567	4.60	0.32	<.2	11	8.81
RO-4	08/19/98	25.0	7.47	558	5.40	<0.01	<.2	10	8.27
RO-4	09/23/98	22.1	7.10	550	5.00	<0.01	<.2	9.30	7.81
RO-4	10/19/98	22.3	7.15	547	5.00	<0.01	0.22	7.70	8.35
RO-4	11/18/98	22.2	7.17	540	5.30	<0.01	<.2	8.70	8.23
RO-4	12/28/98	22.0	7.16	555	4.10	<0.01	<.2	9.10	7.66
RO-4	01/27/99	22.4	7.30	544	5.20	<0.01	<.2	9.50	7.31
RO-4	02/23/99	22.1	7.07	520	6.00	0.10	.4	12	6.66
RO-4	03/23/99	22.9	7.31	534	6.10	<0.01	<.2	13	6.99
RO-4	04/29/99	22.5	7.10	541	5.80	<0.01	<.2	12	6.68
RO-4	05/25/99	22.6	7.10	539	5.60	<0.01	<.2	12	6.15
RO-4	06/30/99	22.5	7.00	533	6.00	0.02	<.2	13	6.06
RO-4	06/30/99	22.5	7.00	533	6.00	0.02	<.2	13	6.06
BH-1	07/08/98	21.9	7.36	502	4.83	0.03	<.2	10	8.07
BH-1	08/17/98	21.1	7.47	502	4.90	0.01	<.2	9.80	7.42
BH-1	09/23/98	22.1	7.30	497	4.85	0.01	<.2	10	7.15
BH-1	10/21/98	21.8	7.47	495	4.90	<0.01	<.2	9.90	8.46
BH-1	11/20/98	21.8	7.36	493	5.10	<0.01	<.2	9.90	ND
BH-1	12/30/98	21.6	7.28	ND	4.10	0.03	<.2	9.80	ND
BH-1	01/28/99	21.7	7.14	490	4.80	<0.01	<.2	10	ND
BH-1	02/23/99	21.7	7.36	490	5.10	0.01	<.2	10	ND
BH-1	03/23/99	21.9	7.51	491	4.90	0.01	<.2	10	ND
BH-1	04/30/99	21.6	7.72	492	4.70	<0.01	<.2	10	ND
BH-1	05/25/99	21.9	7.21	489	4.80	<0.01	<.2	10	ND
BH-1	06/29/99	21.8	7.07	489	5.10	0.02	<.2	5.10	4.93
AC-1	07/07/98	22.4	7.20	558	4.15	0.02	<.2	21	11.83
AC-1	09/29/98	22.6	7.35	553	4.00	0.03	<.2	21	11.78
AC-1	11/02/98	22.6	7.22	555	4.10	0.02	<.2	20	12.10
AC-1	11/20/98	22.5	7.39	554	4.20	<0.01	<.2	20	11.70
AC-1	12/30/98	22.1	7.14	ND	3.50	0.03	<.2	20	10.91
AC-1	01/29/99	23.0	7.22	556	4.70	0.02	<.2	20	9.66
AC-1	02/24/99	22.7	7.21	558	4.40	0.02	<.2	21	9.54
AC-1	03/24/99	22.8	7.54	559	4.50	0.01	<.2	21	9.60
AC-1	04/29/99	22.6	7.42	556	4.20	<0.01	<.2	21	9.09
AC-1	05/25/99	22.8	7.51	560	4.40	<0.01	<.2	21	8.77
AC-1	06/30/99	22.7	7.43	562	4.60	0.03	<.2	21	8.46
ADJK-1	07/07/98	21.5	7.38	346	5.76	0.02	<.2	5.5	12.00
ADJK-1	08/17/98	20.7	7.37	333	4.80	<0.01	<.2	5.2	12.00
ADJK-1	09/22/98	21.5	7.38	333	4.90	0.01	<.2	5.2	11.78
ADJK-1	10/20/98	21.6	7.59	340	5.25	<0.01	<.2	5.6	12.96
ADJK-1	11/19/98	21.7	7.56	338	5.30	<0.01	0.33	5.4	12.65

Table 3. Chemical characteristics and nitrogen species concentrations of monthly ground-water and rainfall samples, and ground-water altitudes for sampled wells

[Units are as follows: °C, degrees Celsius; pH, standard units; SC 9specific conductance) in microsiemens per centimeter; DO (dissolved oxygen) and nitrogen species, milligrams per liter; ND, not determined; NA, not applicable; and RH-FT, Rocky Hill Fire Tower rainfall site]

Site Name	Sample Date	Water temperature, °C	pH	SC	DO	Ammonium Nitrogen	Total Kjeldahl Nitrogen	Nitrate Nitrogen	Ground-water elevation, meters above sea level
ADJK-1	12/29/98	21.7	7.39	ND	4.80	0.01	<.2	5.2	11.92
ADJK-1	01/28/99	21.8	7.47	336	4.90	<0.01	<.2	5.5	11.39
ADJK-1	02/24/99	21.7	7.22	336	4.90	0.01	<.2	5.6	11.58
ADJK-1	03/24/99	21.9	7.75	335	5.30	0.01	<.2	5.3	10.59
ADJK-1	04/30/99	21.7	7.82	334	5.50	0.01	<.2	5.2	10.27
ADJK-1	05/25/99	21.9	7.45	327	5.50	<0.01	<.2	5.0	10.07
ADJK-1	06/29/99	21.8	7.40	328	5.30	0.03	<.2	5.1	9.91
SU-1	07/08/98	21.9	7.22	337	3.89	0.03	<.2	4.2	ND
SU-1	08/17/98	21.6	7.73	264	5.00	0.01	<.2	4.6	ND
SU-1	09/22/98	22.0	6.50	324	4.00	0.01	<.2	5.3	ND
SU-1	10/20/98	22.2	7.64	261	1.70	<0.01	<.2	3.7	ND
SU-1	11/19/98	22.1	7.49	332	2.00	<0.01	0.25	5.1	ND
SU-1	12/29/98	21.9	7.16	ND	4.20	0.02	<.2	5.4	ND
SU-1	01/28/99	21.8	7.54	282	4.80	<0.01	<.2	3.3	ND
SU-1	02/24/99	21.8	7.29	311	3.50	0.01	<.2	4.3	ND
SU-1	03/24/99	22.0	7.66	276	3.90	0.01	<.2	4.7	ND
SU-1	04/30/99	21.8	7.71	367	4.50	<0.01	<.2	5.6	ND
SU-1	05/24/99	22.0	6.99	362	4.80	<0.01	<.2	5.7	ND
SU-1	06/29/99	21.9	7.37	333	4.70	0.03	<.2	5.2	ND
SU-1	06/29/99	21.9	7.37	333	4.70	0.03	<.2	5.2	ND
HD-1	07/07/98	21.1	7.09	348	1.68	0.04	<.2	0.45	5.24
HD-1	08/19/98	21.3	7.43	337	1.85	<0.01	<.2	0.46	5.21
HD-1	09/21/98	21.1	7.06	323	3.60	<0.01	<.2	0.30	5.36
HD-1	10/20/98	22.7	7.33	296	0.40	0.01	<.2	0.25	7.54
HD-1	11/19/98	22.5	7.23	343	2.30	0.01	0.29	0.39	5.43
HD-1	12/29/98	21.7	7.24	344	1.40	0.03	<.2	0.53	5.09
HD-1	01/28/99	22.3	7.02	344	1.30	0.01	<.2	0.50	5.75
HD-1	02/24/99	22.3	6.88	369	2.60	0.01	<.2	0.74	5.53
HD-1	03/24/99	22.1	7.51	364	1.80	<0.01	<.2	0.57	5.19
HD-1	04/30/99	21.8	7.56	354	1.40	<0.01	<.2	0.45	4.86
HD-1	05/25/99	21.9	7.20	356	1.20	<0.01	<.2	0.33	4.79
HD-1	06/29/99	21.7	7.10	358	1.00	0.03	<.2	0.35	4.72
SH-26A	09/23/98	22.4	7.56	474	2.30	0.01	<.2	15	12.95
SH-26A	10/21/98	22.5	7.52	473	2.10	0.01	<.2	14	14.98
SH-26A	11/20/98	22.5	7.57	472	2.10	<0.01	<.2	14	13.58
SH-26A	12/30/98	22.0	7.23	500	2.80	<0.01	<.2	19	12.81
SH-26A	01/29/99	22.5	7.16	496	3.10	<0.01	<.2	19	12.25
SH-26A	02/23/99	22.3	7.61	485	2.80	0.02	<.2	17	12.49
SH-26A	03/25/99	22.5	7.58	468	2.00	<0.01	<.2	14	12.74
SH-26A	04/30/99	22.2	7.73	466	2.10	<0.01	<.2	12	12.40
SH-26A	05/24/99	22.9	7.21	469	2.50	<0.01	<.2	13	12.23
SH-26A	06/30/99	22.9	7.61	466	2.45	0.02	<.2	11	12.15
TM-05	07/21/98	21.9	7.83	284	7.90	0.03	<.2	15	11.86
TM-05	08/20/98	21.4	7.98	263	8.20	<0.01	<.2	14	11.33

Table 3. Chemical characteristics and nitrogen species concentrations of monthly ground-water and rainfall samples, and ground-water altitudes for sampled wells

[Units are as follows: °C, degrees Celsius; pH, standard units; SC 9specific conductance) in microsiemens per centimeter; DO (dissolved oxygen) and nitrogen species, milligrams per liter; ND, not determined; NA, not applicable; and RH-FT, Rocky Hill Fire Tower rainfall site]

Site Name	Sample Date	Water tempera-ture, °C	pH	SC	DO	Ammonium Nitrogen	Total Kjeldahl Nitrogen	Nitrate Nitrogen	Ground-water elevation, meters above sea level
TM-05	09/24/98	22.7	8.22	265	7.90	<0.01	0.29	14	10.85
TM-05	10/19/98	22.4	8.09	285	8.35	<0.01	<.2	15	11.93
TM-05	11/18/98	22.1	8.08	282	8.50	<0.01	<.2	15	11.88
TM-05	12/28/98	21.7	8.08	277	6.30	<0.01	<.2	14	11.27
TM-05	01/27/99	22.3	8.26	273	7.60	0.01	<.2	14	10.82
TM-05	02/23/99	21.7	8.01	271	8.20	0.02	<.2	14	9.97
TM-05	03/23/99	22.5	8.03	281	8.40	<0.01	<.2	15	10.18
TM-05	04/29/99	22.1	8.06	276	7.90	<0.01	<.2	14	9.80
TM-05	05/24/99	22.7	7.26	285	7.90	<0.01	<.2	14	9.58
TM-05	06/28/99	22.0	8.03	289	8.00	0.02	<.2	15	9.36
TM-03	07/22/98	21.5	7.70	329	7.40	0.19	<.2	16	11.57
TM-03	08/20/98	21.5	7.89	327	8.30	<0.01	<.2	15	11.06
TM-03	09/24/98	22.3	8.08	320	7.55	0.01	<.2	16	10.59
TM-03	10/19/98	22.2	7.98	321	8.20	<0.01	<.2	15	11.68
TM-03	11/18/98	22.0	7.91	324	8.55	<0.01	<.2	16	11.63
TM-03	12/28/98	25.0	7.91	324	6.20	<0.01	<.2	16	11.02
TM-03	01/27/99	22.0	7.50	320	8.12	<0.01	<.2	15	10.55
TM-03	02/23/99	21.8	7.86	318	8.00	0.02	<.2	16	9.71
TM-03	03/23/99	22.3	7.97	317	7.80	<0.01	<.2	18	9.92
TM-03	05/24/99	22.4	7.19	323	8.00	<0.01	<.2	17	9.31
TM-03	06/28/99	22.2	7.94	311	7.70	0.03	<.2	16	9.11
DE-02	07/22/98	21.7	7.48	472	4.80	0.05	<.2	20	10.17
DE-02	08/20/98	22.0	7.50	476	6.35	<0.01	<.2	11	9.99
DE-02	09/24/98	21.9	7.56	454	6.20	<0.01	<.2	12	9.95
DE-02	10/19/98	22.3	7.44	486	6.00	<0.01	<.2	12	11.81
DE-02	11/18/98	22.1	7.41	459	6.10	<0.01	<.2	9.9	10.48
DE-02	12/28/98	21.5	7.44	478	4.80	<0.01	<.2	11	9.99
DE-02	01/27/99	21.8	7.71	484	6.30	<0.01	<.2	12	9.85
DE-02	02/23/99	21.2	7.31	487	6.60	0.02	<.2	12	9.43
DE-02	03/23/99	22.2	7.40	488	6.40	<0.01	<.2	12	9.77
DE-02	04/29/99	21.8	7.49	501	6.50	<0.01	<.2	13	9.50
DE-02	05/24/99	22.0	6.80	504	7.00	<0.01	<.2	13	9.31
DE-02	06/28/99	22.3	7.22	520	7.00	0.03	<.2	16	9.10
RHFT	Jul-98	ND	5.75	11	ND	0.03	<.2	0.16	NA
RHFT	Aug-98	ND	3.55	15.5	ND	0.03	.22	0.37	NA
RHFT	Sep-98	ND	6.03	7.1	ND	0.06	<.2	0.09	NA
RHFT	Oct-98	ND	4.98	10	ND	0.09	.2	0.07	NA
RHFT	Nov-98	ND	5.68	14	ND	0.17	.2	0.22	NA
RHFT	Dec-98	19.1	5.79	15	ND	0.31	0.42	0.25	NA
RHFT	Jan-99	ND	5.98	8.8	ND	0.04	<.2	0.12	NA
RHFT	Feb-99	17.0	6.63	0	ND	0.30	0.25	0.44	NA
RHFT	Mar-99	ND	6.54	25	ND	0.30	0.43	0.59	NA
RHFT	Apr-99	ND	5.78	28	ND	0.40	0.65	0.57	NA
RHFT	May-99	27.4	6.79	38	ND	0.70	0.84	0.84	NA
RHFT	Jun-99	22.8	3.84	10.5	ND	0.10	<.2	0.21	NA

Nitrogen Species in Ground Water

Nitrate is by far the dominant form of nitrogen in ground water from all wells sampled during this study (table 3). Nitrate-N concentrations ranged from less than 0.02 to 22 mg/L in water from all wells sampled. Fluctuations in nitrate-N concentrations for water samples from each site are shown in figure 3. Generally, water samples from wells with nitrate-N concentrations higher than 10 mg/L showed the greatest monthly fluctuations (fig. 3a). For example, water samples from six of eight wells (VW-7, RO-4, BH-1, SH-26A, TM-03, and DE-02) had monthly nitrate-N concentrations that varied by at least 5 mg/L during the study period. It is noteworthy that of the two wells located on the same farm, TM-03 and TM-05, water samples from TM-03 showed considerable monthly fluctuations in nitrate-N concentrations whereas monthly nitrate-N concentrations were relatively constant in water samples from TM-05. Water from most wells with lower nitrate-N concentrations (less than 6 mg/L) also showed large monthly fluctuations (fig. 3b). nitrate-N concentrations in water from four sites, VW-2, VW-4, VW-8, and SU-1, showed monthly variations of more than 50 percent.

For the entire data set, there was a very weak, not statistically significant ($r=0.034$; $p=0.70$), correlation between monthly changes in nitrate-N concentrations and corresponding changes in ground-water levels. Statistically significant ($p<0.05$) correlations between nitrate-N concentrations and ground-water levels were found at only three sites (ADJK-1, VW-2, VW-8); however, positive correlations (statistically nonsignificant) between these two variables were found at four other sites (BH-1, HD-1, SH-26A, TM-05). Nonsignificant negative correlations between nitrate-N and ground-water levels were found at six sites (AC-1, DE-02, RO-4, TM-03, VW-4, and VW-7). There was almost no discernable response of nitrate-N concentrations to the large increase in water levels measured at most wells during October 1998. With the exception of decreases in nitrate-N concentrations in water samples from SU-1 and VW-2 in October 1998, nitrate-N concentrations in water samples collected in October and November 1998 showed little or no change relative to September 1998.

Nitrate-N data from monthly ground-water samples collected at SH-26A from a previous study of ground-water quality near dairy farms in the MSRB (Andrews, 1994) were analyzed along with rainfall during the period May 1991 to March 1993 (fig. 4). A comparison of nitrate concentrations and water-level data from Andrews (1994) indicates that monthly nitrate concentrations were lower when ground-water levels rose and highest when ground-water levels were lowest (fig. 4). These results indicate that dilution from increased ground-water recharge likely is an important factor in reducing nitrate concentrations. Andrews (1994) concluded that denitrification reactions were not occurring in ground water at site SH-26A, based on experiments to evaluate factors limiting denitrification in ground water at dairy farms. No significant changes in nitrate concentrations were observed for aliquots from sealed ground-water samples collected during several days. The addition of glucose did result in lower nitrate concentrations and higher nitrite concentrations, leading Andrews (1994) to conclude that denitrification may have been inhibited by the lack of an organic carbon substrate.

There was almost no discernible response of nitrate-N concentrations to monthly changes in dissolved oxygen concentrations. During the study period, ground water at all sites remained aerobic. At seven sites, there was a weak positive correlation between nitrate-N concentrations and dissolved-oxygen concentrations; however, the correlation between these two variables was statistically significant ($p<0.05$) at only two sites (RO-4 and TM-05). At site VW-8, a statistically significant negative correlation ($p<0.001$) was found between nitrate concentrations and dissolved oxygen.

Large increases or decreases in nitrate-N concentrations could have resulted from various agricultural practices (fertilizer application and animal-waste management) at each site. For example, nitrate-N concentrations in water samples from DE-02 decreased from 20 to 11 mg/L from July to August 1998, rose slightly in September and October and generally remained the same through May 1999, then rose sharply to 16 mg/L in June 1999. These changes most likely are related to manure spreading on a nearby pasture and the presence or absence of poultry litter stockpiles near the sampled well. During a 1992-93 study of poultry operations and their effect on nitrate concentration in ground water from this farm, Hatzell (1995) noted that increases in organic nitrogen associated with increases in nitrate-N concentrations probably were related to the presence of litter stockpiles and downward percolating rainwater that may have leached nitrate from the litter stockpiles out of the soil profile. Concentrations of nitrate-N in water samples from DE-02 were considerably higher in

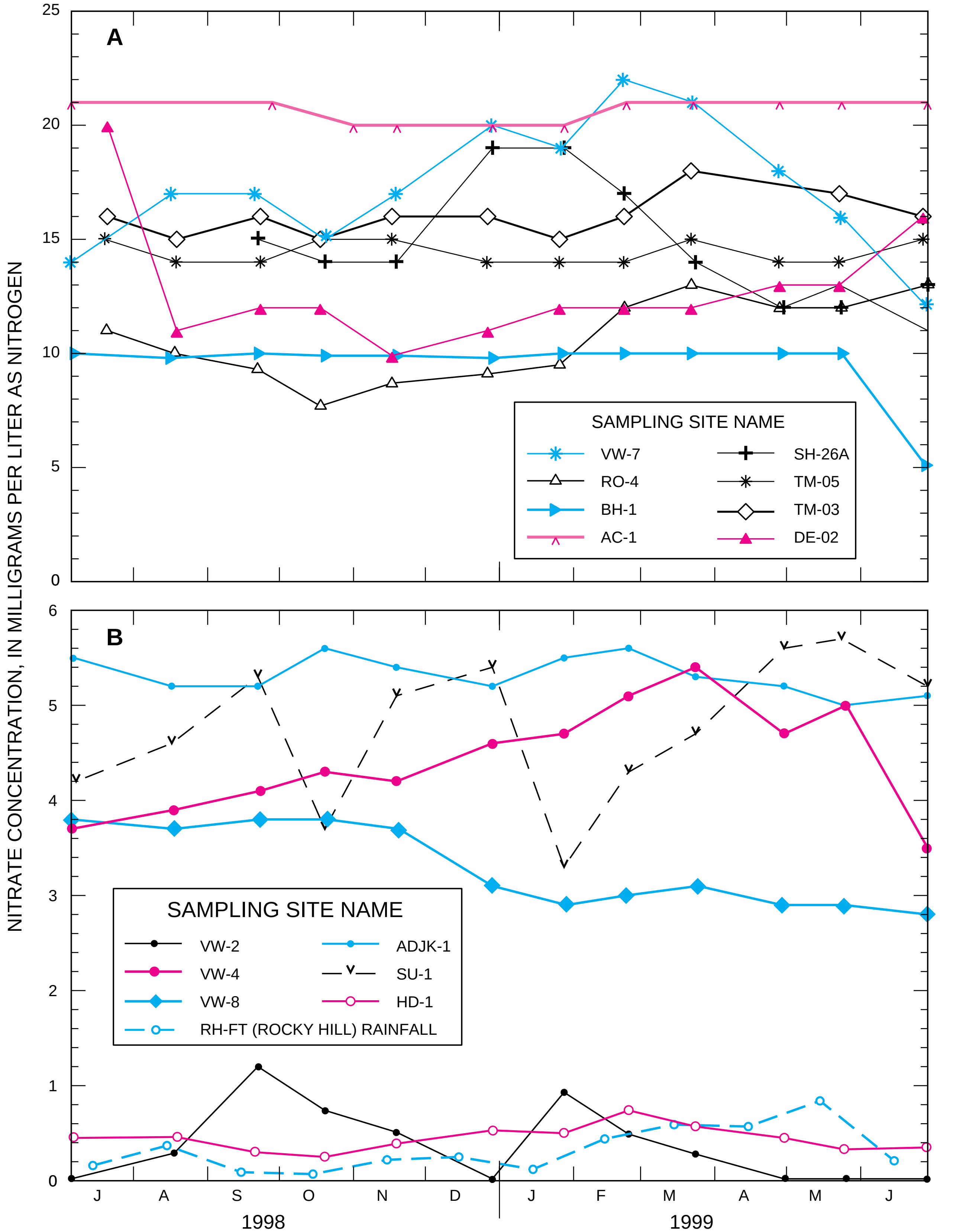

Figure 3. Fluctuations in nitrate-N concentrations in water samples from wells in Suwannee and Lafayette Counties, July 1998 to June 1999, (a) sites with higher nitrate concentrations, (b) sites with lower nitrate concentrations.

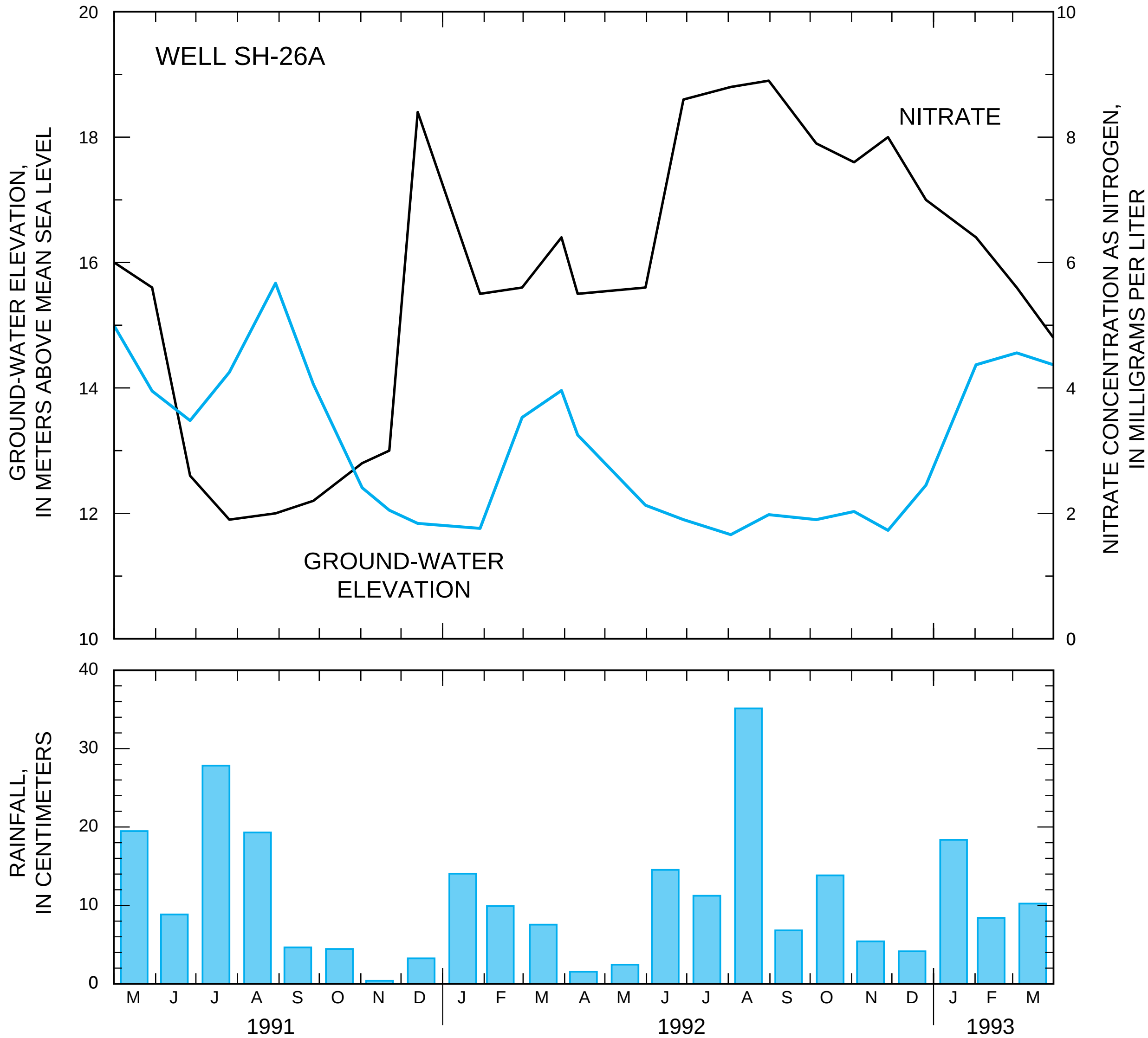

Figure 4. Changes in nitrate-N concentrations in water samples from well SH-26A during 1991 through 1993.

1998-99 (9.9 to 20 mg/L) than those measured in 1992 by Hatzell (1995), which ranged from 0.8 to 2.6 mg/L, and may be indicative of the cumulative effect of manure spreading during the intervening 6 to 7 years. At another poultry farming operation, nitrate-N concentrations increased from 16 to 18 mg/L in water samples from site TM-03 during February and March 1999, and this change likely is related to the application of litter to the fallow field in March 1999. The subsequent planting of corn seemed to have a very small effect on the nitrate concentrations in water from this well during May and June 1999. Hatzell (1995) noted similar nitrate-N concentrations and a link to poultry-waste management practices on nitrate-N concentrations for this site. A similar increase in nitrate-N concentrations was seen in water samples at RO-4 from February to March 1999, and likely is related to the application of fertilizer to cropland in the vicinity of this well.

Nitrogen Species in Rainfall

For most monthly composite rainfall samples, nitrate was the dominant N species. However, in rainfall samples collected in November and December 1998, and in April and May 1999, ammonium-N (NH_4^+, the ionized form of ammonia in acidic rainfall) concentrations were similar or greater than nitrate-N concentrations (RH-FT in table 3). High ammonium concentrations may indicate that volatilization of ammonia from fertilizers and animal wastes are occurring in the MSRB and this ammonia is being incorporated in rainfall. To test this possibility, nitrate-N and ammonium-N concentrations in monthly rainfall samples collected at the Rocky Hill site (RH-FT), a site surrounded by forested and agricultural land, were compared with mean monthly volume-weighted concentrations of nitrate-N and ammonium-N in samples collected at Bradford Forest, a forested, non-agricultural site 100 km east of the study area and part of the National Atmospheric Deposition/ National Trends Network (http://nadp.sws.uiuc.edu). Similar nitrate-N and ammonium-N concentrations were observed between the two sites during June, August, September, and November 1998, and during January and June 1999 (fig. 5a). During February through May 1999, however, nitrate-N and ammonium-N concentrations were substantially higher in samples collected from the Rocky Hill site compared to those collected during the same months at a site at Bradford Forest (fig. 5a). Total N deposition rates in kilograms per hectare, calculated from the sum of nitrogen and ammonium and multiplied by the amount of rainfall in each month, are considerably higher for the Rocky Hill site than the Bradford Forest site during February through June 1999 (fig. 5b). The higher nitrogen concentrations and total N (nitrate plus ammonium) deposition rate at the Rocky Hill site in Suwannee County may indicate that substantial amounts of ammonia are volatilized from fertilizers, released to the atmosphere, and incorporated in rainfall as ammonium and nitrate.

COMPARISON OF GROUND-WATER CHEMISTRY DURING WET AND DRY CONDITIONS

Ground-water samples were collected in March 1998 during high-flow conditions for the Suwannee River and in November during low-flow conditions (fig. 6). Water types remained similar for the samples from eight wells collected during high water-table conditions (March 1998) and lower water-table conditions (November 1998). For ground-water samples from most sites, Ca, Mg-HCO_3 (calcium, magnesium-bicarbonate) was the dominant water type, although water samples from two sites had a Ca-HCO_3 type (SU-1 and VW-4). Dissolved-solids concentrations were similar in samples collected from most wells, with the exception of SU-1, HD-1, and BH-1 where dissolved-solids concentrations were at least 30 percent lower in March than in November 1998. Ground-water levels measured in all wells were substantially higher in March than in November, and differences from March to November ranged from 0.14 (VW-7) to 6.53 m (HD-1). Above normal rainfall accounted for the increase in water levels in March, with 76.7 cm of rainfall measured at Mayo, Fla., during November 1997 through February 1998. This rainfall amount is 39.3 cm above the normal amount recorded at this station during 1960-90 (Owenby and Ezell, 1992).

Stable Isotopes of Oxygen, Hydrogen, and Carbon

Stable isotopes of oxygen ($\delta^{18}O$) and hydrogen (δD) were used in this study to determine the origin of water and to characterize possible mixing of different sources of water in the aquifer. Values of $\delta^{18}O$ and δD in water samples from wells cluster along the global meteoric water line (Craig, 1961), $\delta D = 8\delta^{18}O + 10$, (fig. 7), which indicates that springs receive ground water that is recharged from rainfall, which undergoes little or no evaporation. The more or less random deviations from the meteoric water line indicate that the spring waters are little affected by evaporation or mixing with surface waters that would have an enriched isotopic signature due to evaporation. The observed small differences in isotopic composition likely are related to storm track origin, number of evaporation and condensation cycles (Dansgaard, 1964), and the temperature of infiltrating rain in the recharge areas for the wells. Similar values of $\delta^{18}O$ and δD were observed for monthly samples of rainfall collected from June 1995 through May 1996 at the Rocky Hill Fire Tower (RH-FT) (Katz and others, 1998). These monthly samples were composited from weekly samples collected using a wet/dry atmospheric deposition collector. Values of δD and $\delta^{18}O$ are slightly enriched (higher) in water sampled from AC-1 and VW-2 (fig. 7), indicating that water recharging the aquifer at this site may have undergone some evaporation or that mixing has occurred with surface water that contains an enriched isotopic signature.

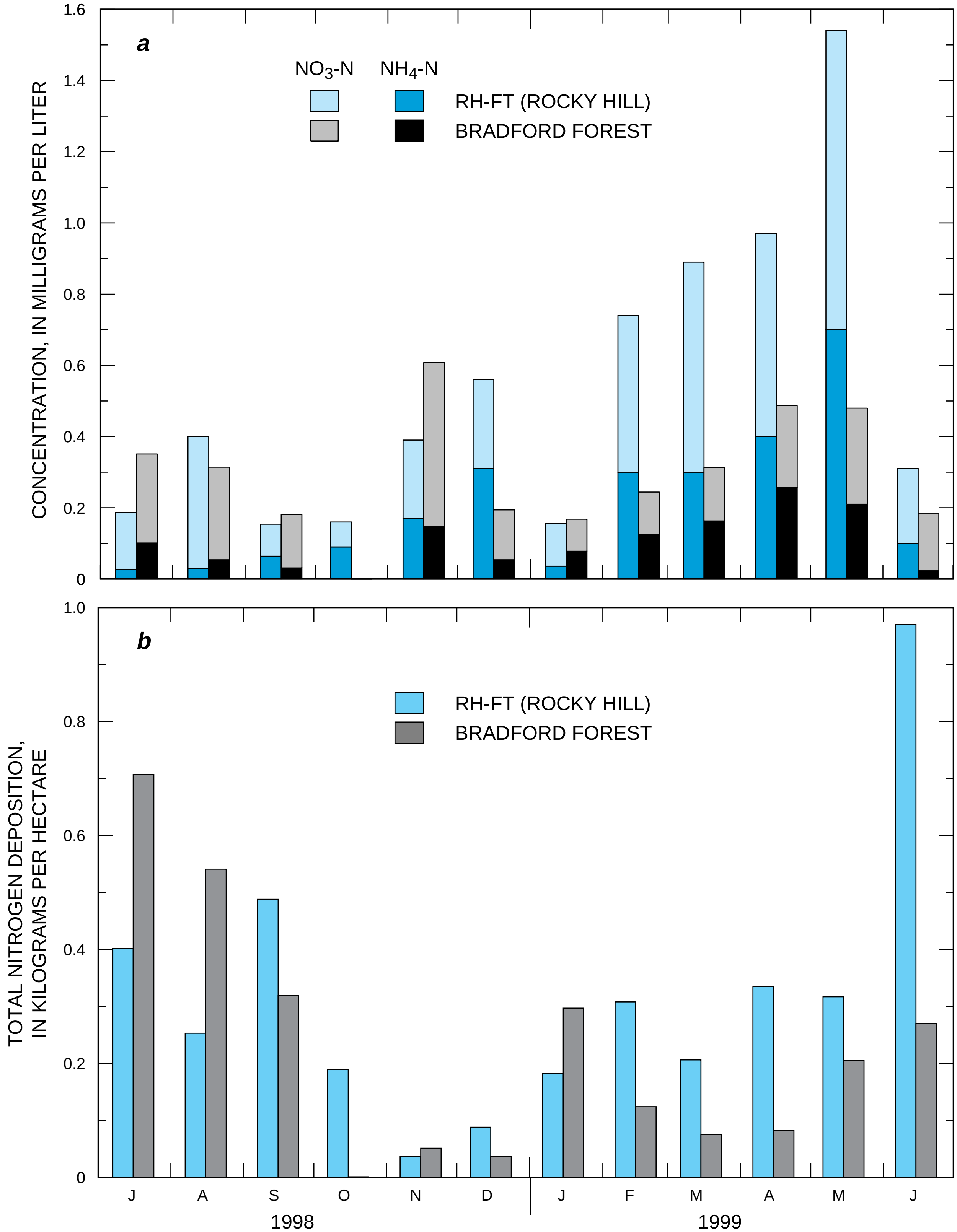

Figure 5. Comparison of nitrate and ammonium concentrations (a) and nitrogen deposition in rainfall collected at Rocky Hill and Bradford Forest sites (b).

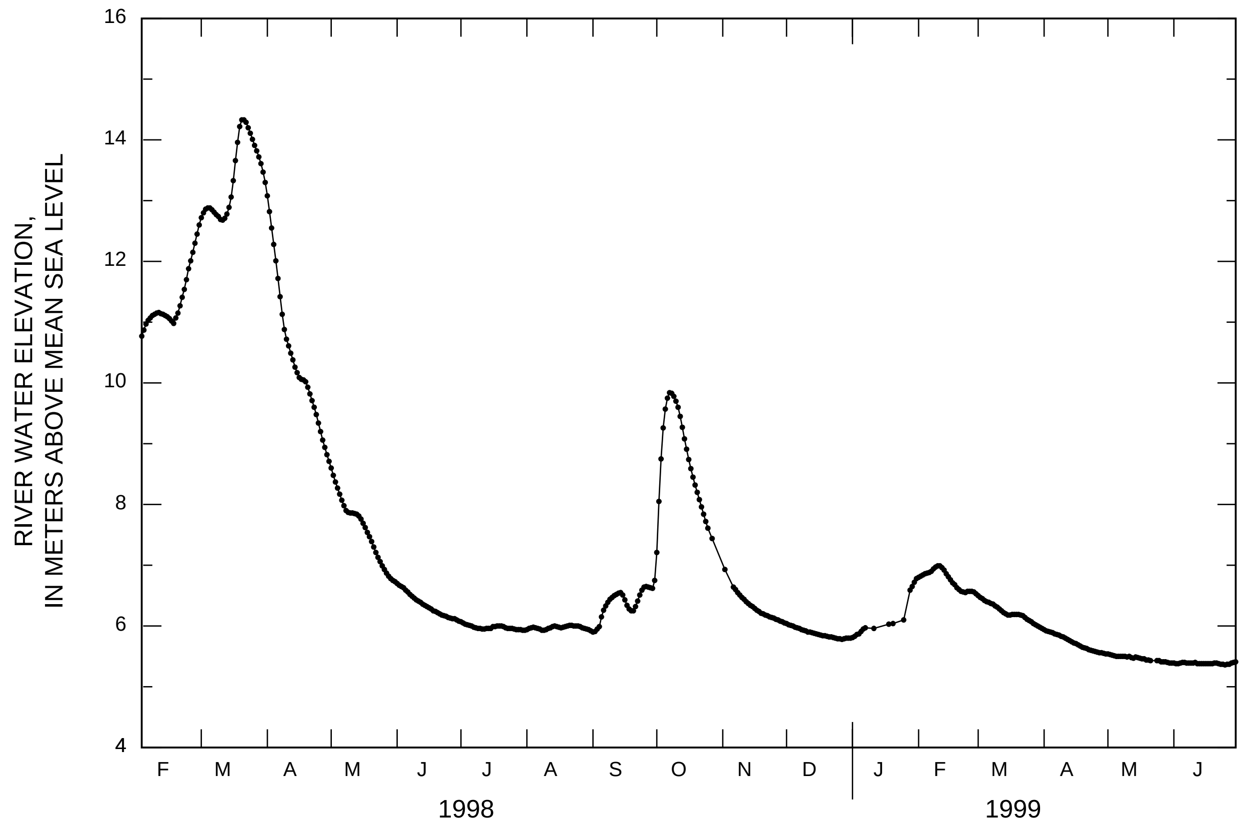

Figure 6. Water-level elevation of Suwannee River at Luraville, Florida, February 1998 through June 1999.

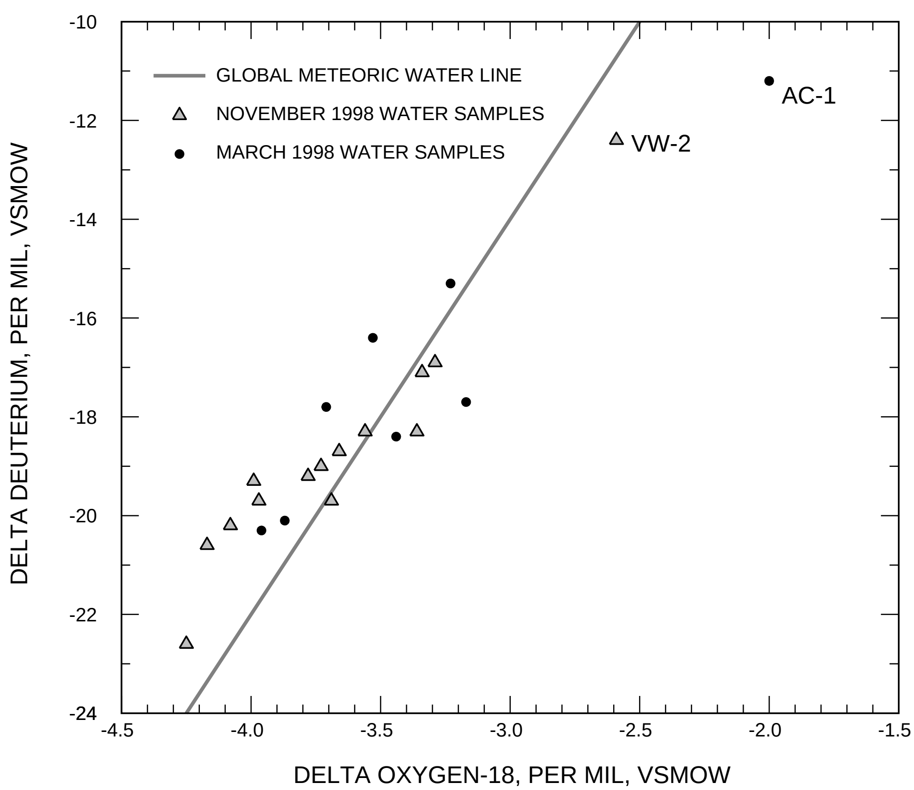

Figure 7. Deuterium and oxygen-18 content of ground-water samples collected in March and November 1998 compared to the global meteoric water line.

Carbon isotopic ($\delta^{13}C$) compositions of ground-water samples ranged from –8.5 to –13.7 per mil (table 4). These values are enriched in carbon-13 relative to water from the surficial aquifer system ($\delta^{13}C$ = -18 to –25 per mil) in northern Florida (Katz and others, 1998). Ground water in the MSRB evolves under open carbon dioxide conditions where heterotrophic bacteria in the unsaturated zone aerobically degrade dissolved organic carbon in interstitial waters ($\delta^{13}C$ = -24 per mil) to produce carbon dioxide (CO_2) that has a slightly enriched $\delta^{13}C$ content (Deines, 1980). The variations in $\delta^{13}C$ values in ground water arise from different amounts of CO_2 resulting from degradation of organic carbon and from dissolution of calcite ($\delta^{13}C$ = 0 per mil), according to the following reaction:

$$CaCO_3 + H_2CO_3 = Ca^{2+} + 2HCO_3^-$$

$\delta^{13}C$ values were similar in March and November 1998 for water samples collected from each of the eight wells sampled (table 4). The greatest difference in $\delta^{13}C$ values between the March and November water samples was observed at site HD-1, with the March sample depleted about 1.3 per mil compared to the sample collected in November 1998. The lower $\delta^{13}C$ value most likely resulted from mixing of river water ($\delta^{13}C$ value of about -24 per mil (Katz and others, 1998)) with ground water.

Dissolved Gases in Ground Water

Dissolved-gas data, particularly argon (Ar) and nitrogen (N_2), can provide valuable information on recharge processes in ground-water systems. The solubilities of Ar and N_2 vary substantially as a function of temperature (Weiss, 1970); consequently, the concentrations of these gases in ground water indicates the temperature of the unsaturated zone during recharge. The recharge-water temperature and amounts of excess air (Heaton and Vogel, 1981) can be evaluated from a plot of dissolved Ar against N_2 concentrations (Busenberg and others, 1993) for samples of ground water collected in March 1998 (fig. 8). Solubilities of Ar and N_2, are shown between 0 and 30 ^{o}C at sea level along the zero-excess-air line, which is labeled as water in equilibrium with air. The 5, 10, 15, and 20 lines represent the equilibrium concentrations of Ar and N_2 with 5, 10, 15, and 20 cubic centimeters per liter (cm^3/L) of air added in excess of the equilibrium concentrations. Other information on the evolution of dissolved gases can be obtained from this plot. For example, addition of radiogenic Ar will shift the sample composition vertically as shown in the lower right corner of the plot (fig. 8). Denitrification reactions involving microbially mediated reduction of nitrate to N_2 will shift the dissolved-gas composition horizontally. Excess air added during recharge processes will shift the composition diagonally. The recharge-water temperature of a sample plotted on figure 8 is obtained by extending a diagonal line parallel to the excess air lines from the sample to the recharge-water temperature axis on the right-hand side of the diagram (Busenberg and others, 1993). The excess-air content of the sample is obtained by following a diagonal line (parallel to the excess-air lines) from the sample to the excess-air axis on the top of the diagram.

The concentrations of N_2 and Ar in most ground-water samples from March 1998 are consistent with atmospheric equilibration during ground-water recharge with minor amounts of excess air added either during recharge or as a result of sampling methods. The apparent recharge temperatures for most samples are 22 ±3^{o}C (assuming 10-12 m elevation for recharge and 100 percent humidity at the water table) with about 0-7 cm^3/L of excess air during recharge. These calculated temperatures agree closely with a mean annual air temperature of 20.4^{o}C at Live Oak for 1961-90 (Owenby and Ezell, 1992). Also, $\delta^{15}N$ values of dissolved N_2 generally are consistent with air equilibration during recharge and with minor amounts of excess air (0.6 to 0.8 per mil).

Ground-water samples from AC-1 have slightly lower $\delta^{15}N$ (N_2) values (0.3 to 0.4 per mil) that could indicate small amounts of nonatmospheric N_2; however, some of those samples may have leaked slightly. Also, water from well AC-1 appears most likely to have excess N_2, based on the isotope and N_2 concentration data (possibly as much as 2 to 3 mg/L). Further evidence for denitrification in the aquifer at AC-1 is provided by $\delta^{15}N$-NO_3 values, which are presented in the next section of this report.

With the exception of water from well AC-1, denitrification reactions likely have not reduced nitrate concentrations in this ground-water system. Mixing of surface water and ground water at site HD-1 is evident from dissolved N_2 and Ar data (fig. 8). The calculated average recharge temperature for water from HD-1 is 12.5^{o}C, which is considerably lower than recharge temperatures calculated for other water samples. During this time period, the river water temperature was approximately 12 ^{o}C.

Table 4. Concentrations of major elements, nitrogen species, and selected isotopes in water from wells sampled in March and November 1998

[All concentration units are in milligrams per liter unless otherwise noted; SC (specific conductance) is reported as microsiemens per centimeter; DO, dissolved oxygen; DS, dissolved solids; DOC, dissolved organic carbon; ND, not determined; shaded rows indicate high-flow conditions; TU, tritium units; <, less than]

Site Name	Sampling Date	"Temp, °C"	SC	DO	pH	Ca	Mg	Na	K	Cl	SO4	F	HCO3	SiO2	NH4-N	TKN	NO3-N	PO4	DS	DOC	Tannic acid	$\delta^{13}C$ per mil	$\delta^{2}H$ per mil	$\delta^{18}O$ per mil	$\delta^{15}N$ per mil	^{3}H, TU
VW-2	11/19/98	23.2	338	0.10	7.30	47	13	3	0.4	4.7	1.8	0.15	207	7.2	0.1	0.26	0.51	0.04	172	0.2	<0.1	-9.9	-12.4	-2.6	9.7	ND
VW-4	03/10/98	22.6	387	2.35	7.18	64	5.1	5.7	2.4	11.0	20	<0.1	178	5.5	0.036	<0.2	4.2	0.18	195	<0.1	<0.1	-10.5	-15.3	-3.2	8.9	ND
VW-4	11/19/98	22.5	370	3.10	7.40	62	4.3	4.9	1.9	9.8	18	<0.1	171	5.3	<0.01	<0.2	4.2	0.05	185	<0.1	<0.1	-10.3	-18.3	-3.4	7.6	ND
VW-7	03/09/98	23.0	319	1.52	7.27	62	18	7.6	4.9	16.0	15	0.13	224	4.9	0.024	<0.2	10	0.03	235	0.2	<0.1	-8.9	-17.7	-3.2	10.2	6.6
VW-7	11/20/98	23.0	542	4.40	7.30	57	22	10	6.2	12.0	15	0.13	219	7.2	<0.01	0.34	17	0.35	231	<0.1	<0.1	-8.9	-19.2	-3.8	10.6	ND
VW-8	03/10/98	22.0	341	1.48	7.42	47	11	3.6	0.9	6.1	12	0.12	169	4.8	0.032	<0.2	4.3	0.04	164	<0.1	<0.1	-11.4	-18.4	-3.4	5.9	ND
VW-8	11/20/98	21.7	324	1.20	7.60	45	10	3.7	0.8	6.0	12	0.1	158	4.4	<0.01	<0.2	3.7	0.04	156	<0.1	<0.1	-12.0	-17.1	-3.3	5.9	ND
RO-4	11/18/98	22.2	540	5.30	7.20	97	4.1	4.8	3.0	12.0	26	<0.1	244	6.3	<0.01	<0.2	8.7	0.02	270	<0.1	<0.1	-13.7	-19.7	-4.0	3.8	ND
BH-1	03/11/98	21.7	507	4.20	7.16	37	12	3.8	1.7	5.9	9.5	0.17	152	6.1	0.027	<0.2	3.9	0.53	146	<0.1	<0.1	-10.6	-16.4	-3.5	9.6	ND
BH-1	11/20/98	21.8	493	5.10	7.40	60	17	7.5	5.0	15.0	15	0.12	219	4.7	<0.01	<0.2	9.9	0.04	227	<0.1	<0.1	-10.2	-18.7	-3.7	9.3	ND
AC-1	03/09/98	22.3	500	2.14	7.00	65	14	6.4	4.9	11.0	18	0.11	200	6.3	0.094	<0.2	13	0.03	218	<0.1	<0.1	-8.5	-11.2	-2.0	12.8	3.1
AC-1	11/20/98	22.5	554	4.20	7.40	70	16	7.7	7.0	14.0	21	<0.1	195	6.3	<0.01	<0.2	20	0.03	231	<0.1	<0.1	-9.4	-16.9	-3.3	11.7	ND
ADJK-1	03/11/98	21.5	376	5.27	7.10	53	11	4.1	1.0	9.1	8.1	0.11	179	6.2	0.026	0.32	6.5	0.03	175	0.1	<0.1	-11.1	-20.3	-4.0	7.3	ND
ADJK-1	11/19/98	21.7	338	5.30	7.60	46	11	3.9	0.9	8.0	8.5	0.1	158	6.0	<0.01	0.33	5.4	0.03	157	<0.1	<0.1	-11.1	-19.3	-4.0	7.0	ND
SU-1	03/11/98	21.0	201	0.17	7.41	31	5.2	3.2	1.0	5.3	5.8	0.1	105	5.0	0.022	0.49	0.8	0.04	103	7.6	1.9	-11.6	-17.8	-3.7	5.4	ND
SU-1	11/19/98	22.1	332	2.00	7.50	54	4.2	6.6	0.8	10.0	14	<0.1	146	6.6	<0.01	0.25	5.1	0.04	162	<0.1	<0.1	-11.8	-19.0	-3.7	5.5	ND
HD-1	03/16/98	18.3	216	0.09	7.08	28	9.5	3.3	0.8	5.0	4.2	0.17	122	5.1	0.044	0.51	0.02	0.04	111	7.9	2.4	-13.4	-20.1	-3.9	1.7	3.8
HD-1	11/19/98	22.5	343	2.30	7.20	49	12	2.6	0.5	4.9	6.9	0.15	207	6.9	<0.01	0.29	0.39	0.02	175	<0.1	<0.1	-12.1	-18.3	-3.6	6.3	ND
SH-26A	11/20/98	22.5	472	2.10	7.60	63	14	5.5	1.9	10.0	11	0.15	195	5.0	<0.01	<0.2	14	0.03	203	<0.1	<0.1	-11.3	-19.7	-3.7	5.6	ND
TM-05	11/18/98	22.1	282	8.50	8.10	30	11	4.1	0.2	6.6	3	0.14	82	5.4	<0.01	<0.2	15	0.03	95	<0.1	<0.1	-9.4	-20.6	-4.2	6.0	ND
TM-03	11/18/98	22.0	324	8.60	7.90	36	13	4.6	0.5	6.8	3.8	0.14	106	5.5	<0.01	<0.2	16	0.04	117	<0.1	<0.1	-9.8	-22.6	-4.3	7.2	ND
DE-02	11/18/98	22.1	459	6.10	7.20	55	19	5.9	1.0	9.0	17	0.19	207	5.4	<0.01	<0.2	9.9	0.01	210	<0.1	<0.1	-12.2	-20.2	-4.1	10.9	ND

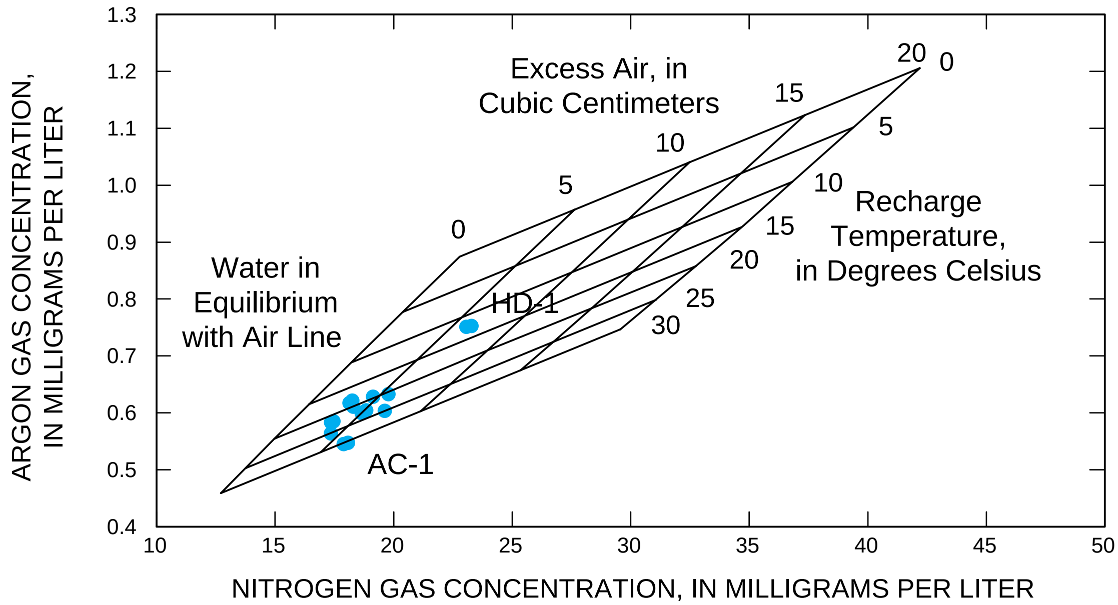

Figure 8. Nitrogen and argon gas concentrations in water from wells.

Ground-water samples were not analyzed for dissolved gases during dry conditions in November 1998. Ground water discharging from springs in the MSRB, however, was sampled for dissolved gases during low-flow conditions for the Suwannee River in July 1997 and August 1998 (Katz and others, 1999), and these conditions likely were similar to those during November 1998. Dissolved-gas data for water samples from these springs indicate that concentrations of N_2 and Ar are consistent with atmospheric equilibration during ground-water recharge with minor amounts of excess air added during recharge or as a result of sampling methods (Katz and others, 1999). No excess N_2 was found in these spring waters, and apparent recharge temperatures were 21 ±2.5^{o}C.

Concentrations of Nitrogen Species in Ground Water

Nitrate-N concentrations in ground water in March 1998 compared to November 1998 were substantially lower in samples from five wells (VW-7, AC-1, BH-1, SU-1, and HD-1), slightly higher in two wells (VW-8 and ADJK-1), and remained the same in well VW-4 (table 4). Generally, the largest decreases in nitrate concentrations from low-flow to high-flow conditions were observed in wells that had the largest increase in water levels: AC-1, BH-1, and HD-1; showing increases in ground-water levels of 2.39, 3.46, and 6.53 m, respectively. The March 1998 water level however, was 4.3 m higher in well VW-8 than in November, but the nitrate concentration was higher in March than in November (4.3 to 3.7 mg/L).

A noteworthy observation is that NH_3-N concentrations were higher in water samples collected in March than in November, regardless of whether nitrate increased (VW-8 and ADJK-1), decreased (VW-4, BH-1, AC-1, SU-1, and HD-1) or remained the same (VW-4). The increase in ammonia-N concentrations in water from some wells may be related to leaching of ammonia from fertilizers or manure applied to the land surface that infiltrated the soil during periods of high rainfall. In other sites, reduction of small amounts of nitrate from denitrification reactions may result in increased ammonia concentrations.

A previous study in Lafayette County (Katz and others, 1997) concluded that the ground-water flow system was more sluggish during high-flow conditions in March 1991 compared to lower water-table conditions in June 1990. Ground-water levels in 1991 increased by as much as 6 m at some wells following 3 months of above normal rainfall, compared to water levels in 1990 (near normal rainfall). Hydraulic heads in the aquifer, however, were less than the hydrostatic pressure of the Suwannee River. These conditions, along with substantially reduced amounts of dissolved oxygen in the aquifer, and increased amounts of organic carbon and other reduced species that could serve as electron donors, created conditions favorable for the natural reduction of nitrate in ground water by denitrification reactions (Korom, 1992). Whereas increases in pH, calcium, and bicarbonate were observed in the previous study that compared ground water chemistry in 1991 to 1990 (Katz and others, 1997), similar changes in ground-water chemistry (increased calcium and bicarbonate concentrations during high-flow conditions) were not observed in this study.

Analyses for dissolved nitrogen gas and $\delta^{15}N$ of N_2 indicate that denitrification may be occurring in the aquifer at site AC-1; however, the availability of dissolved oxygen makes denitrification reactions unlikely in the aquifer at other sites. The hydraulic gradient decreases during high-flow conditions (Katz and others, 1997) resulting in a more sluggish flow system. Increased recharge to the aquifer, however, also occurs and likely results in an accompanying dilution effect, which results in lower nitrate concentrations in the aquifer. Decreases in dissolved oxygen during high-flow conditions in March 1998 were observed in water samples from six of the eight wells sampled during low-flow and high-flow conditions (table 4). At four of these wells, however, dissolved-oxygen concentrations in ground water were above 1.5 mg/L, whereas three sites (VW-2, SU-1, and HD-1) had dissolved oxygen concentrations below 0.2 mg/L. Water samples also had elevated DOC and tannic-acid concentrations from two wells (SU-1 and HD-1), which were not observed at any other sites (table 4). River water with high organic carbon concentrations (Katz and others, 1997; Crandall and others, 1999) could provide organic carbon needed for denitrification, although, organic carbon derived from the limestone may serve as another electron donor source (Foster and others, 1985). Even though dissolved oxygen concentrations at SU-1 and HD-1 were low, no evidence for denitrification was found from dissolved N_2 gas data. Dilution effects probably resulted in lower nitrate concentrations as indicated by a corresponding decrease in chloride concentrations from 10 to 5.3 mg/L at SU-1 and a constant chloride concentration (5.0 and 4.9 mg/L) at HD-1. Concentrations of Ca, Mg, SO_4, HCO_3 also were substantially lower during high-flow conditions compared to low-flow conditions in water samples at SU-1 and HD-1. At the other six sites, chloride concentrations decreased at two wells (AC-1 and BH-1) but increased at four wells (VW-4, VW-7, VW-8, and ADJK-1).

SOURCES OF NITRATE IN GROUND WATER BENEATH DIFFERENT LAND USES

Values of $\delta^{15}N$ of nitrate ($\delta^{15}N\text{-}NO_3$) have been used to identify sources of nitrate contamination in ground water since the mid-1970's (Heaton, 1986). The method has been used succesfully in areas with thin and permeable unsaturated zones with a shallow water table (Kreitler, 1975; Heaton, 1986) and in mantled karst aquifers (Wells and Krothe, 1989; Andrews, 1994; Hornsby, 1994). Low $\delta^{15}N\text{-}NO_3$ values (0 to 3 per mil) generally indicate an inorganic nitrate source (artificial or synthetic fertilizer); whereas higher $\delta^{15}N\text{-}NO_3$ values (10 to 20 per mil) generally indicate an organic source of nitrate (for example, animal wastes from manure spreading, human wastes from septic-tank effluent). Delta $^{15}N\text{-}NO_3$ values that fall between 3 and 10 per mil likely are indicative of mixed inorganic and organic sources of nitrate or a soil organic nitrogen source. Delta $^{15}N\text{-}NO_3$ values for rainfall generally are within the range of –12 to +2 per mil (Heaton, 1986).

Nitrogen Isotope Data

Generally, no trend was observed between the concentration of nitrate and $\delta^{15}N\text{-}NO_3$ values in ground-water samples (fig. 9), indicating that concentrations of nitrate in shallow parts of the Upper Floridan aquifer likely are not altered after recharge. A trend of higher $\delta^{15}N\text{-}NO_3$ values corresponding to lower nitrate concentrations would indicate that denitrification reactions may be occurring. At site AC-1, however, $\delta^{15}N\text{-}NO_3$ values were higher in March 1998 than in November 1998 when lower nitrate concentrations were observed. Reduction of nitrate by the denitrification process would result in a higher $\delta^{15}N\text{-}NO_3$ value, as the ligher isotope of nitrogen (^{14}N) is preferred in the microbial reaction that transforms nitrate to reduced nitrogen species.

Water from wells VW-7 and AC-1 in Lafayette County had relatively high $\delta^{15}N\text{-}NO_3$ values, 10.6 and 11.7 per mil in November 1998, respectively (table 4), indicating the likelihood of an organic (animal waste) source of nitrate. Even though nitrate concentrations decreased substantially in water from these two wells following a period of sustained rainfall, the $\delta^{15}N\text{-}NO_3$ value decreased only slightly to 10.2 per mil in water from well VW-7 and increased to 12.8 per mil in AC-1

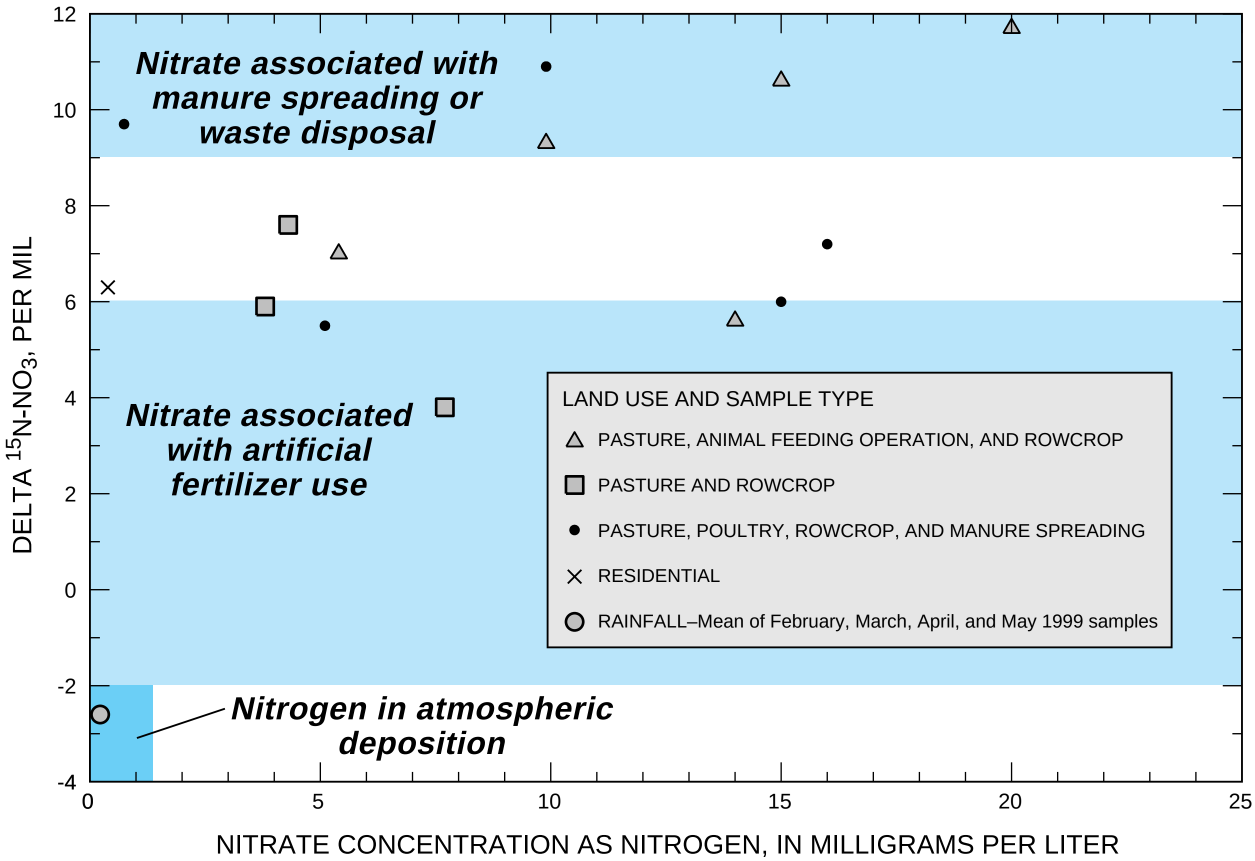

Figure 9. Delta nitrogen-15 of nitrate and nitrate-N concentrations in water from wells sampled in November 1998 and in rainfall.

in March 1998. These wells are located near, and downgradient from, dairy and poultry farms where leachate from animal wastes could have contributed nitrate to ground water. Water samples from three other wells, VW-2, BH-1, and DE-02, also had $\delta^{15}N\text{-}NO_3$ values above 9 per mil indicating the likelihood of an organic source of nitrogen. Water samples from wells HD-1 and RO-4 had $\delta^{15}N\text{-}NO_3$ values less than 4 per mil (1.7 and 3.8 per mil, respectively), indicating an inorganic nitrogen source; RO-4 is located near a fertilized field. The low value for HD-1 sampled in March 1998, likely results from a mixture of ground water and surface water with an assumed low $\delta^{15}N\text{-}NO_3$ value similar to rainfall.

Four rainfall samples from RH-FT were analyzed for $\delta^{15}N$ of nitrate. Delta $^{15}N\text{-}NO_3$ values for monthly composite rainfall samples were –3.6, -1.8, -2.2, and –2.8 per mil for February, March, May, and June 1999, respectively. Although these ranges could be due to natural variations, the lower value for February also could be indicative of higher amounts of ammonia volatilization from fertilizers and animal wastes in the study area. Isotopic shifts of several per mil, however, can occur during a single storm event and between consecutive rain storms (Heaton, 1986), so the monthly $\delta^{15}N\text{-}NO_3$ value represents a mean of several storms with possibly different isotopic values. Seasonal variations in $\delta^{15}N$ of nitrate in rain also may indicate seasonal differences in the chemical reactions by which nitrate ions are formed (Calvert and others, 1985), rather than differences in the predominant source of nitrogen gases in the atmosphere.

Different waste-management practices and other land uses at farms with animal husbandry operations can result in multiple sources of nitrogen (inorganic and organic), which are indicated by $\delta^{15}N\text{-}NO_3$ values between 5 and 9 per mil. For example, sites SU-1 (5.5 per mil), TM-03 (7.2 per mil), and TM-05 (6.0 per mil), are located on farms where manure from chicken houses and synthetic fertilizers are both added to fields. Typically, liquid ammonia fertilizer is applied to fields after each of three coastal hay cuttings per year at a rate of approximately 90 kilograms of nitrogen per hectare. In contrast, site DE-02 is located on a farm where only manure from chicken houses is spread on fields twice a year and the resulting $\delta^{15}N\text{-}NO_3$ value is 10.9 per mil (organic nitrogen). Site SH-26A ($\delta^{15}N\text{-}NO_3$ of 5.6 per mil) is located near a dairy farm where effluent from a wastewater lagoon used to collect wastes from the dairy feedlot is sprayed onto crop fields, which are supplemented with applications of synthetic fertilizers.

Identifying the sources of nitrate at specific sites is further complicated by other sources of nitrogen in the vicinity of the sampled wells. For example, nitrogen may be leaching from waste-disposal pits and septic tanks or from small domestic-waste disposal plants (Hatzell, 1995). Local flow patterns, which can differ subsantially from regional flow patterns, can have a profound influence on the movement of nitrate from off-site sources relative to on-site sources of nitrogen.

Nitrogen isotope values obtained in this study correspond to the range in values obtained from previous studies in the basin. Andrews (1994) concluded that the source of nitrate in shallow ground water tended to be leachate from livestock waste, whereas the source of nitrate in deeper ground water was attributed to leachate from synthetic fertilizers. Other studies have noted $\delta^{15}N\text{-}NO_3$ values of 10 per mil and higher and have attributed those values to organic sources of nitrogen (N) from dairy or poultry operations (Hornsby, 1994; Katz and others, 1999). Hornsby (1994) also reported that most wells sampled in the MSRB (44 of 66) yielded water with $\delta^{15}N\text{-}NO_3$ values that were less than or equal to 2 per mil, indicating that inorganic nitrogen (synthetic fertilizers) and (or) soil nitrogen was the dominant source of nitrogen. The depth of these 66 wells ranged from 14 to 44 m (median depth 27 m) below land surface, and water samples from these wells were withdrawn from zones about 5 to 40 m below the top of the Upper Floridan aquifer. Therefore, Hornsby's (1994) samples may not represent the most recent nitrate contamination.

Factors Affecting Timing of Nitrogen Recharge to Ground Water

Nitrogen attributed to manure spreading may enter the aquifer shortly after application to the land surface. In previous studies, an increase in organic nitrogen from less than 0.2 to 0.65 mg/L was found about 3 months after application of poultry litter to fallow fields (Hatzell, 1995); however, concentrations had decreased to background levels within 9 months following the litter application. The source of the increase in organic nitrogen may have been from the decomposition of the poultry litter or related to the decomposition of soil organic matter, which can occur while a field is prepared for planting (Stevenson, 1982). No increase in nitrate-N concentrations were observed after litter application, which may have been due to nitrate uptake by the corn plants or an insufficient amount of time for nitrate to move from the soil to the ground water (Hatzell, 1995).

Peak nitrate-N concentrations in water samples from several wells (RO-4, TM-03, TM-05, and VW-4) occurred in March 1999, indicating that some nitrate from fertilizer applications in February or early March could possibly take about 1 month to move through the unsaturated zone into the aquifer. At some farms, however, fertilizers are applied after each hay cutting; an increase in ground-water nitrate concentrations may not have resulted because the amount of recharge was small due to insufficient rainfall or because evapotranspiration rates were higher during the summer. Another possibility is that some nitrogen could move into ground water in the form of organic nitrogen or ammonia, and mineralization to nitrate could be occurring in ground water. There is a sufficient amount of dissolved oxygen for this reaction to occur in the aquifer. The possibility also exists that increases in nitrate concentrations seen in water samples collected in March 1999 could have resulted from fertilizer applied during the 6 to 12 months prior to sampling. Based on the short-term variations of major ion and nutrient concentrations shown in tables 2 and 3, however, and those found in other studies (such as Andrews, 1994; Hatzell, 1995), this possibility is rather remote.

SUMMARY AND CONCLUSIONS

During July 1998 through June 1999, water samples were collected monthly from 14 wells and an atmospheric deposition collector as part of a cooperative study between the Florida Department of Environmental Protection and the U.S. Geological Survey. The study was designed to evaluate temporal variability and sources of nitrate concentrations in ground water beneath various land-use types in the Middle Suwannee River Basin (MSRB) in northern Florida. Changes in nitrogen species, and the chemical and isotopic composition of ground water also were evaluated at eight sites during low-flow and high-flow conditions for the Suwannee River.

An unusually high amount of rainfall (43.5 centimeters) in September and October 1998 resulted in an increase in ground-water levels in all wells in October. During the remainder of the study period, monthly rainfall was considerably below mean monthly values measured at Live Oak, Fla., during the period 1961-90. During November 1998 through May 1999, rainfall was 40.7 centimeters below mean monthly rainfall values. There were no statistically significant differences in monthly values for field parameters (pH, specific conductance, dissolved oxygen, and temperature) with the exception of pH, which may have been related to the use of different meters and probes during the study period.

The presence of karst features (sinkholes, springs, solution conduits) and the relatively thin sands that overlie the limestone provide for rapid movement of water containing elevated nitrate concentrations to the Upper Floridan aquifer, which is the source of water supply in the MSRB. Nitrate was the dominant form of nitrogen in ground water from all sites, and nitrate-N concentrations ranged from less than 0.02 to 22 mg/L as nitrogen. Water samples from most wells showed substantial monthly or seasonal fluctuations in nitrate-N concentrations. Generally, water samples from wells with nitrate-N concentrations higher than 10 mg/L showed the greatest monthly fluctuation. For example, water samples from six of eight wells had monthly nitrate-N concentrations that varied by at least 5 mg/L during the study period. Water from most wells with lower nitrate-N concentrations (less than 6 mg/L) also showed large monthly fluctuations. For instance, nitrate concentrations in water from four sites showed monthly variations of more than 50 percent. Statistically significant correlations between nitrate concentrations and ground-water levels were found at only three sites. Large increases or decreases in nitrate concentrations likely result from various agricultural practices (fertilizer application and animal waste management) at each site. For example, an increase in nitrate-N in March, which was observed at several sites, most likely results from application of synthetic fertilizers during the late winter months. Decreases in nitrate-N concentrations at a poultry farm site are related to the timing of chicken manure spreading on a nearby pasture.

For most monthly samples of rainfall, nitrate-N was the dominant nitrogen species; however, ammonium-N concentrations were similar or greater than nitrate-N during November and December 1998, and April and May 1999. During February through May 1999, both nitrate-N and ammonium-N concentrations were substantially higher in monthly rainfall samples collected at the study area site than at a National Atmospheric Deposition Program/National Trends Network site in Bradford Forest, located approximately 100 km east of the study area. Corresponding nitrogen deposition rates also were higher in the study area than those at Bradford Forest. The higher nitrogen concentrations and deposition rates in the middle Suwannee River Basin may indicate that substantial amounts of ammonia are volatilized from fertilizers, released to the atmosphere, and incorporated in rainfall as ammonium and nitrate.

Even though ground-water levels were substantially higher in March 1998 than in November 1998, water types (calcium, magnesium-bicarbonate) remained similar for samples collected from the eight wells during high-flow (March 1998) and low-flow conditions (November 1998). Comparing data collected in March 1998 to November 1998, nitrate-N concentrations were lower in water samples from five wells, slightly higher in two wells, and remained the same in one well. Evidence for reduction of nitrate due to denitrification reactions at site AC-1 was indicated by higher concentrations of nitrogen gas in ground-water samples from AC-1 compared to other sites, and a corresponding increase in nitrogen isotope values of nitrate with a decrease in nitrate concentrations for water samples collected in March compared to November 1998. Denitrification is unlikely at other sites based on the presence of dissolved oxygen concentrations greater than 2 mg/L in water from most wells, little or no dissolved organic carbon, and the lack of a relation between nitrate concentrations and nitrogen isotope values. Mixing of river water with ground water was evident at two sites (HD-1 and SU-1) based on substantial increases in dissolved organic carbon and tannic acid concentrations in water collected during high-flow conditions compared to low-flow conditions.

Nitrogen isotope data indicated that fertilizers and animal wastes were dominant sources at some sites. For example, water samples from two wells had $\delta^{15}N\text{-}NO_3$ values less than 4 per mil, indicating an inorganic nitrogen source such as synthetic fertilizer. These sites are located near row-crop fields where fertilizers are applied. In contrast, water samples from five sites had $\delta^{15}N\text{-}NO_3$ values greater than 9 per mil, indicating the likelihood of an organic (animal waste) source. These sites are located near dairy and poultry farming operations, where leachate from animal wastes likely contributes nitrate to ground water. Different waste-management practices and multiple land uses at farms resulted in water samples with $\delta^{15}N\text{-}NO_3$ values (5 to 9 per mil) that fell between these two end members.

Monthly variations of nitrate concentrations in ground water likely are related to land-use practices. Increases in nitrate concentrations during the spring of 1999 seem to be related to applications of fertilizer and manure on fields used for row crops and hay. Nitrate concentrations did not respond to increases in water levels in October 1998 due to unusually high amounts of rainfall in September and October 1998 (43.5 cm total for both months). Short-term and seasonal fluctuations in nitrate concentrations are substantial in ground water in the study area, and the magnitude of these fluctuations need to be taken into account when assessing possible trends in the improvement or degradation of ground-water quality.

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